PHILOSOPHICAL

TRANSACTIONS

OF THE

ROYAL SOCIETY

OF

LONDON.

FOR THE YEAR MDCCCLX.

VOL. 150.

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MDCCCLXI.

PHILOSOPHICAL TRANSACTIONS

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ROYAL SOCIETY

OF

LONDON,

FOR THE YEAR MDCCXCI.

PART I.

LONDON:

ADVERTISEMENT.

THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions*, take this opportunity to acquaint the Public, that it fully appears, as well from the Council-books and Journals of the Society, as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication, than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the Public, that their usual meetings were then continued, for the improvement of knowledge, and benefit of mankind, the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed, to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings, contained in the several papers so published, which must still rest on the credit or judgement of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body, upon any subject, either of Nature or Art, that comes before them. And therefore the

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thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.

The Meteorological Journal hitherto kept by the Assistant Secretary at the Apartments of the Royal Society, by order of the President and Council, and published in the Philosophical Transactions, has been discontinued. The Government, on the recommendation of the President and Council, has established at the Royal Observatory at Greenwich, under the superintendence of the Astronomer Royal, a Magnetical and Meteorological Observatory, where observations are made on an extended scale, which are regularly published. These, which correspond with the grand scheme of observations now carrying out in different parts of the globe, supersede the necessity of a continuance of the observations made at the Apartments of the Royal Society, which could not be rendered so perfect as was desirable, on account of the imperfections of the locality and the multiplied duties of the observer.

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Page 743, line 9, *for* 774 indicated horse-power *read* 744 indicated horse-power.

—— 744, line 9, after the words marine boilers, *insert* the engine had been in some respects modified by the makers, Messrs. J. M. ROWAN and Co.; and in particular, a surface condenser designed by them had been substituted for the former surface condenser.

ERRATUM IN VOL. 150.

Page 283, line 21, *for* DELIQUIERE *read* LEREILLÉ.

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Adjudication of the Medals of the Royal Society for the year 1860 by the President and Council.

The Copley Medal to Professor Robert Wilhelm Bunsen, of Heidelberg, Foreign Member of the Royal Society, for his Researches on Cacodyl, Gaseous Analysis, the Volcanic Phenomena of Iceland, and other Researches.

A Royal Medal to Mr. William Fairbairn, F.R.S., for his various Experimental Inquiries on the Properties of the Materials employed in Mechanical Construction, contained in the Philosophical Transactions and in the Publications of various Scientific Societies.

A Royal Medal to Dr. Augustus V. Waller, F.R.S., for his Investigations into the Anatomy and Physiology of the Nervous System, and for the introduction of a valuable Method of conducting such investigations.

The Rumford Medal to Professor J. Clerk Maxwell, for his Researches on the Composition of Colours, and other Optical Papers.

The Bakerian Lecture was delivered by Mr. William Fairbairn, F.R.S., and entitled "Experimental Researches to determine the Density of Steam at all Temperatures, and to determine the Law of Expansion of Superheated Steam."

The Croonian Lecture was delivered by Mr. James Pettigrew, and entitled "On the Arrangement of the Muscular Fibres of the Ventricular Portion of the Heart of the Mammal."

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PHILOSOPHICAL TRANSACTIONS.

I. *On the Analytical Theory of the Attraction of Solids bounded by surfaces of a hypothetical Class including the Ellipsoid.* *By* W. F. Donkin, *M.A., F.R.S., F.R.A.S., Savilian Professor of Astronomy in the University of Oxford.*

Received September 2,—Read December 8, 1859.

The following investigation is the result of an attempt to simplify the analytical treatment of the problem of the Attraction of Ellipsoids. The application to this particular case, of certain known propositions relating to closed surfaces in general, showed that the principal theorems could easily be deduced without taking account of any other properties of the ellipsoid than those expressed by two differential equations, of which the truth is evident on inspection. In fact if we take the equation

$$\frac{x^2}{a^2+h}+\frac{y^2}{b^2+h}+\frac{z^2}{c^2+h}=k,$$

we see at once that the expression on the left side, considered as a function of x, y, z, h, satisfies the two partial differential equations

$$\frac{d^2u}{dx^2}+\frac{d^2u}{dy^2}+\frac{d^2u}{dz^2}=2\left(\frac{1}{a^2+h}+\frac{1}{b^2+h}+\frac{1}{c^2+h}\right)$$

$$\left(\frac{du}{dx}\right)^2+\left(\frac{du}{dy}\right)^2+\left(\frac{du}{dz}\right)^2+4\frac{du}{dh}=0,$$

and these equations express all that we require to know about the ellipsoid, except the fact that the surface is capable of being extended to infinity in every direction by the variation of h, without ceasing to be closed. But it appeared also that the success of the method depended only on the circumstance that the right-hand member of the first equation, and the coefficient of $\frac{du}{dh}$ in the second, are constants independent of k. It was therefore possible to generalize the process by taking indeterminate functions of h for these two constants. As, however, the coefficient of $\frac{du}{dh}$ could always be reduced to a

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constant independent of h, by taking a function of h as a parameter instead of h, we may suppose, without loss of generality, that this reduction has been effected.

Mr. CAYLEY has shown*, in the latest publication on this subject which I have met with, that if *two* of the principal theorems of attraction (in the case of the ellipsoid) be given, the rest follow very simply, and are common to all surfaces of which those two can be predicated†. But the demonstration of the two assumed theorems constitutes the most essential part of the analytical problem, and it is my present object to show that they, and the others connected with them, are implied in the two differential equations above written.

1. Suppose the equation

$$F(x, y, z, \theta)=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

represents closed surfaces for all values of the parameter θ within certain limits; and let the surface corresponding to any particular value θ_1 of θ, be called "the surface θ_1." With reference to these surfaces let the limits of integrals be indicated thus: $[\ ]^{\theta}$ signifies that an integral enclosed between the brackets, if it consist of *superficial* elements, is extended over the surface θ; if of *solid* elements, through the whole space within that surface. In either case let $[\ ]_{\theta_0}^{\theta_1}$ stand as an abbreviation for $[\ ]^{\theta_1}-[\ ]^{\theta_0}$.

Let

$$\left\{\left(\frac{dv}{dx}\right)^2+\left(\frac{dv}{dy}\right)^2+\left(\frac{dv}{dz}\right)^2\right\}^{\frac{1}{2}}$$

be, for shortness, denoted by Q_v (whatever v may be).

Let us put also

$$\left(\frac{d}{dx}\right)^2+\left(\frac{d}{dy}\right)^2+\left(\frac{d}{dz}\right)^2=D^2,$$

and let the element of surface be called $d\sigma$.

By means of (1.) we may suppose θ expressed as a function of x, y, z. On this supposition we have

$$Q_\theta=\left\{\left(\frac{d\theta}{dx}\right)^2+\left(\frac{d\theta}{dy}\right)^2+\left(\frac{d\theta}{dz}\right)^2\right\}^{\frac{1}{2}}.$$

Let the sign of the right-hand member of this equation be so taken that $Q_\theta d\theta$ shall be positive or negative according as the surface $(\theta+d\theta)$ is without or within the surface θ.

Since $Q_\theta^{-1}d\theta$ is the normal thickness at any point of the infinitesimal shell included between the two surfaces θ and $\theta+d\theta$, the latter surface must be either wholly within or wholly without the former, unless Q_θ become infinite at some point of the surface θ, a supposition which it is not *necessary* to exclude, but which I suppose to be excluded for the sake of simplicity.

2. The preliminary propositions to be demonstrated in this article are not new. I am not certain to whom they are originally due; they were, however, employed by Pro-

* See also Camb. Math. Journal, vol. iii. p. 75 for the year 1842.—*Note added June 25*, 1860.

† Note on the Theory of Attraction (Quarterly Journal of Mathematics, vol. ii. p. 338). The two theorems are those marked V. and VI. in this paper.

fessor W. THOMSON in an early volume of the Cambridge Mathematical Journal (to which I have not at present the opportunity of referring) in some form equivalent to (if not identical with) that in which they are here given. They depend on the most elementary principles, and ought to be so well known as to make a demonstration needless; however, I give one for the sake of completeness. Retaining the suppositions of the last article, we have, if P be any function of x, y, z,

$$\left[\iiint \frac{dP}{dx}\,dxdydz\right]^{\theta}=\left[\int \frac{P}{Q_\theta}\frac{d\theta}{dx}\,d\sigma\right]^{\theta}$$

(by integrating the expression on the left with respect to x, and applying a well-known transformation to the double integral).

Let then u be any function of x, y, z, and put

$$p=u\frac{d\theta}{dx}-\theta\frac{du}{dx},\quad q=u\frac{d\theta}{dy}-\theta\frac{du}{dy},\quad r=u\frac{d\theta}{dz}-\theta\frac{du}{dz},$$

then

$$\frac{dp}{dx}+\frac{dq}{dy}+\frac{dr}{dz}=u\mathrm{D}^2\theta-\theta\mathrm{D}^2u;$$

and if the two members of the last equation be multiplied by $dxdydz$, and integrated through the space within the surface θ_1, the result on the left is

$$\left[\int\frac{1}{Q_\theta}\left(p\frac{d\theta}{dx}+q\frac{d\theta}{dy}+r\frac{d\theta}{dz}\right)d\sigma\right]^{\theta_1};$$

or, if p, q, r be replaced by their values, it is

$$\left[\int uQ_\theta d\sigma\right]^{\theta_1}-\left[\int\frac{\theta}{Q_\theta}\left(\frac{du}{dx}\frac{d\theta}{dx}+\frac{du}{dy}\frac{d\theta}{dy}+\frac{du}{dz}\frac{d\theta}{dz}\right)d\sigma\right]^{\theta_1};$$

but in the last of these integrals θ has the same value θ_1 throughout the integration, and may therefore be put outside the integral sign; and the integral which it multiplies is then evidently equivalent to the triple integral $\left[\iiint \mathrm{D}^2u\,.\,dxdydz\right]^{\theta_1}$, since it would be obtained by one integration of each of the three terms of the latter. Hence we have, finally,

$$\left[\int uQ_\theta d\sigma\right]^{\theta_1}=\theta_1\left[\iiint \mathrm{D}^2u\,.\,dxdydz\right]^{\theta_1}+\left[\iiint(u\mathrm{D}^2\theta-\theta\mathrm{D}^2u)dxdydz\right]^{\theta_1},\quad\ldots\ldots\quad(2.)$$

and, subtracting this from the similar equation referring to another value θ_2 of θ,

$$\left[\int uQ_\theta d\sigma\right]^{\theta_2}_{\theta_1}=\theta_2\left[\iiint \mathrm{D}^2u\,.\,dxdydz\right]^{\theta_2}-\theta_1\left[\iiint \mathrm{D}^2u\,.\,dxdydz\right]^{\theta_1}+\left[\iiint(u\mathrm{D}^2\theta-\theta\mathrm{D}^2u)dxdydz\right]^{\theta_2}_{\theta_1},\quad(3.)$$

which last might have been obtained at once by taking the triple integrals through the space included between the surfaces θ_1, θ_2. It is of course necessary for the validity of each equation, that the functions under the integral signs should not become infinite at any point within the limits of the integrations.

3. Let the equation

$$f(x, y, z, h, k)=0\quad\ldots\ldots\ldots\ldots\quad(4.)$$

represent closed surfaces for all values, within certain limits, of the parameters h, k. Let the surface corresponding to a particular pair of values h, k, be called "the surface

h, k;" and let the space (or solid) included between the surfaces (h_1, k), (h_2, k) be called "the shell $\left(\begin{matrix}h_2\\h_1\end{matrix}, k\right)$"; similarly, let that included between the surfaces (h, k_1), (h, k_2) be called "the shell $\left(h, \begin{matrix}k_2\\k_1\end{matrix}\right)$*." Let it also be supposed that each of the surfaces $(h, k+dk)$, $(h+dh, k)$, is either wholly within or wholly without the surface (h, k).

By virtue of equation (4.) either parameter may be considered a function of x, y, z, and the other parameter. Let the function on the left of (4.) be such that when k is considered as a function of x, y, z, h, the two following partial differential equations are satisfied:—

$$\left.\begin{aligned}&\frac{d^2k}{dx^2}+\frac{d^2k}{dy^2}+\frac{d^2k}{dz^2}=\varphi(h)\\&\left(\frac{dk}{dx}\right)^2+\left(\frac{dk}{dy}\right)^2+\left(\frac{dk}{dz}\right)^2+n\frac{dk}{dh}=0\end{aligned}\right\}, \qquad (5.)$$

where $\varphi(h)$ is a function of h not containing k, and n is a constant, independent of h and k.

The second of these equations may be put in another form thus: considering h as implicitly a function of x, y, z, k, we have

$$\frac{dk}{dx}+\frac{dk}{dh}\cdot\frac{dh}{dx}=0, \text{ \&c.},$$

whence

$$\left(\frac{dk}{dx}\right)^2+\left(\frac{dk}{dy}\right)^2+\left(\frac{dk}{dz}\right)^2=\left(\frac{dk}{dh}\right)^2\left(\left(\frac{dh}{dx}\right)^2+\left(\frac{dh}{dy}\right)^2+\left(\frac{dh}{dz}\right)^2\right),$$

or (extracting the root and employing the notation explained in art. 1)

$$Q_k=-\frac{dk}{dh}\cdot Q_h\dagger;$$

hence the second of equations (5.), which is

$$Q_k^2+n\frac{dk}{dh}=0,$$

may be changed into $Q_k \cdot Q_k=n$. In this form it will be actually employed, so that the two equations may be written as follows:—

$$\left.\begin{aligned}&D^2k \quad =\varphi(h)\\&Q_k \cdot Q_k=n\end{aligned}\right| \qquad (6.)$$

* I borrow this notation, with a slight alteration, from Mr. CAYLEY.

† The negative sign must be taken for the following reason: $\frac{dk}{dh}$ is the ratio of corresponding variations of k, h, when the surface passes through a *given* point (x, y, z); now suppose that an increase of h alone, or of k alone, would cause a displacement of the surface, relatively to that point, of the same kind; *i. e.* that the point would be inside the altered surface in both cases, or outside in both cases; then Q_h, Q_k have the same sign (art. 1). But on this supposition, if h and k vary together so that the surface continues to pass through the point (x, y, z), it is plain that h must increase if k decrease, and *vice versâ*, so that $\frac{dk}{dh}$ is negative. Similarly, if Q_h, Q_k have opposite signs, $\frac{dk}{dh}$ is positive. The equation in the text is therefore always true.

4. Now let the general equation (2.), art. 2, be applied to the case of the surface considered in the last article, k being taken for the parameter θ, so that $D^2\theta$ is D^2k, and is $=\varphi(h)$; also let the arbitrary function u be put $=1$, so that $D^2u=0$. Then, observing the second of equations (6.), we obtain from (2.),

$$n\left[\int\frac{d\sigma}{Q_h}\right]^k=\varphi(h)\left[\iiint dxdydz\right]^k.$$

Let the volume enclosed by the surface (h, k) be represented by V. Then, since the normal thickness at any point of the shell $\left(\begin{matrix}h+dh\\h\end{matrix}, k\right)$ is $\frac{dh}{Q_h}$, the above equation is equivalent to

$$n\frac{dV}{dh}=\varphi(h).V,$$

from which we obtain by integration, putting for shortness $e^{\frac{1}{n}\int\varphi(h)dh}=\psi(h)$,

$$V=F(k).\psi(h), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.)$$

where $F(k)$ is an unknown function of k, independent of h.

But if, instead of putting $u=1$, we suppose u to be the potential, at the point (x, y, z), of a given mass M exterior to the surface (h, k), then we have (since D^2u is again $=0$)

$$n\left[\int\frac{ud\sigma}{Q_h}\right]^k=\varphi(h).\left[\iiint udxdydz\right]^k;$$

and if V be put for the potential on M of a (homogeneous) solid bounded by the surface (h, k), this equation is equivalent to

$$n\frac{dV}{dh}=\varphi(h).V,$$

and therefore, as before,

$$V=F(k).\psi(h), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.)$$

where $\psi(h)$ is the same as before, but $F(k)$ is a new unknown function of k, which will also involve the given quantities which define M.

From (7.) and (8.) we have

$$V=\frac{F(k)}{F(k)}.V,$$

which equation expresses

THEOREM I. *The potential, on a given external mass, of a homogeneous solid bounded by the surface* (h, k), *varies as the mass of the solid, if* h *vary while* k *remains constant.*

5. If we put $V(h, k)$ for the volume, and $V(h, k)$ for the potential, denoted above simply by V and V, we obtain from equations (7.) and (8.) the following:—

$$\frac{V(h_2, k_2)-V(h_2, k_1)}{V(h_1, k_2)-V(h_1, k_1)}=\frac{V(h_2, k_2)-V(h_2, k_1)}{V(h_1, k_2)-V(h_1, k_1)},$$

which expresses

THEOREM II. *The potentials, on a given external mass, of the homogeneous shells* $\left(\begin{matrix}h_2, k_2\\h_1, k_1\end{matrix}\right)$, $\left(\begin{matrix}h_1, k_2\\h_1, k_1\end{matrix}\right)$, *are proportional to the masses of the shells.*

When the thickness of the shells is infinitesimal, this proposition may be enunciated as

THEOREM III. *The potential, upon a given external mass, of the homogeneous shell* $\left(\mathrm{h}, \frac{\mathrm{k}+\mathrm{dk}}{\mathrm{k}}\right)$, *varies as the mass of the shell, if* h *vary while* k *remains constant.*

6. The above conclusions were deduced from equation (2.), art. 2. Let us now take equation (3.) and apply it in a similar manner, taking for the parameter θ, no longer k, but an indeterminate function of h (not containing k), say

$$\theta = f(h).$$

This gives, without ambiguity of sign,

$$\mathrm{Q}_\theta = f'(h)\mathrm{Q}_h$$

(for by the convention made, art. 1, as to the signs of Q_h, &c., Q_θ and Q_h must have the same sign or not, according as $f'(h)$ is positive or negative).

Hence, writing the left-hand side of (3.) in full, and introducing the second of the conditions (6.), we have

$$nf'(h_2)\left[\int\frac{ud\sigma}{\mathrm{Q}_h}\right]^{h_2} - nf'(h_1)\left[\int\frac{ud\sigma}{\mathrm{Q}_h}\right]^{h_1} = \left[\iiint u\mathrm{D}^2 f(h).dxdydz\right]_{h_1}^{h_2} + (\text{terms involving } \mathrm{D}^2 u).$$

Now let u be the potential of a given mass M exterior to both the surfaces (h_1, k), (h_2, k), so that $\mathrm{D}^2 u$ is $=0$ throughout the integrations. The integral $\left[\int\frac{ud\sigma}{\mathrm{Q}_k}\right]^k$ is evidently $\frac{d\mathrm{V}}{dk}$, if V be the potential on M of a homogeneous solid (density $=1$) bounded by the surface (h, k); and by equation (8.), art. 4, $\frac{d\mathrm{V}}{dk} = \mathrm{F}'(k).\psi(h)$.

The above equation thus becomes

$$n\mathrm{F}'(k)\{f'(h_2)\psi(h_2) - f'(h_1)\psi(h_1)\} = \left[\iiint u\mathrm{D}^2 f(h).dxdydz\right]_{h_1}^{h_2}.$$

The function $f(h)$ has been so far arbitrary. Let us now determine it in such a manner that $f'(h)\psi(h) =$ a constant independent of h and k; or

$$f(h) = \mathrm{A} + \mathrm{B}\int\frac{dh}{\psi(h)}$$

(A, B being two such arbitrary constants). Then the left-hand side of the equation vanishes; therefore the right-hand side vanishes also, or

$$\left[\iiint u\mathrm{D}^2 f(h).dxdydz\right]_{h_1}^{h_2} = 0;$$

but since u is the potential of an arbitrary mass, this cannot be unless $\mathrm{D}^2 f(h) = 0$. We may therefore (introducing the value of $\psi(h)$, art. 4, and including the arbitrary constants under the integral signs) enunciate

THEOREM IV. *If* f(h) *be defined by the equation*

$$f(h) = \int dh.e^{-\frac{1}{n}\int\alpha\lambda(\alpha)\lambda},$$

then f(h) *satisfies the equation*

$$\mathrm{D}^2 f(h) = 0.$$

This result may be verified by actual differentiation, as will be shown afterwards (art. 12).

7. Resuming the equation (3.), art. 2, and supposing that θ is the function $f(h)$ determined in the last article, so that $D^2f(h)=0$, let us put $u=1$; then the equation becomes

$$f'(h_2)\left[\int\frac{d\sigma}{Q_k}\right]^{h_2}-f'(h_1)\left[\int\frac{d\sigma}{Q_k}\right]^{h_1}=0;$$

if this be multiplied by dk, it expresses the following proposition:—

If the homogeneous infinitesimal shell $\left(\mathrm{h},\ \frac{\mathrm{k}+\mathrm{dk}}{\mathrm{k}}\right)$ *have the density* f'(h), *the mass of the shell is independent of* h.

It follows that the potential of such a shell, on a given *interior* mass, vanishes when h has the value which makes the surface (h, k) extend to infinity in all directions; for the mass of the shell is finite, but every part of it is infinitely distant from the attracted mass.

8. Instead of putting $u=1$, as in the last article, let us now take for u the potential of a given mass M, placed *anywhere*. Then if ϱ be the density, at the point (x, y, z), of the matter composing M, we shall have

$$D^2u=-4\pi\varrho.$$

Let the surface (h_1, k) be within the surface (h_2, k), and let M_1 be all that part of M which is within the former surface, and M_2 all that part which is within the latter (so that M_2 includes M_1).

Also let $f(h)$ be still taken for θ, in equation (3.), art. 2; then $D^2\theta=0$, and the last term on the right of that equation becomes

$$4\pi\left[\iiint\varrho f(h)dxdydz\right]_{h_1}^{h_2}.$$

Now the whole mass included between the two surfaces is M_2-M_1; hence the above integral is equal to

$$4\pi(M_2-M_1)f(h),$$

in which h is put for the parameter of some surface (h, k), which lies between (h_1, k) and (h_2, k), and cuts the mass M_2-M_1. If the mass M be concentrated at a point between the two surfaces, then h is the parameter of the surface (h, k) which passes through that point.

In the general case, however, equation (3.) becomes

$$nf'(h_2)\left[\int\frac{ud\sigma}{Q_k}\right]^{h_2}-nf'(h_1)\left[\int\frac{ud\sigma}{Q_k}\right]^{h_1}=-4\pi M_2f(h_2)+4\pi M_1f(h_1)+4\pi(M_2-M_1)f(h).$$

Let V_1, V_2 be put for the potentials on M of the two infinitesimal shells $\left(h_1, \frac{k+dk}{k}\right)$, $\left(h_2, \frac{k+dk}{k}\right)$, with densities $f'(h_1)$, $f'(h_2)$ respectively; then this equation, multiplied by dk, gives

$$V_2-V_1=\frac{4\pi}{n}\left(-M_2f(h_2)+M_1f(h_1)+(M_2-M_1)f(h)\right)dk. \quad . \quad . \quad . \quad . \quad . \quad (9.)$$

Suppose now that the mass M is unity, and is concentrated at a point *between* the two surfaces, then $M_1=0$, $M_2=1$, and (9.) becomes

$$V_2-V_1=\frac{4\pi dk}{n}\big(f(h)-f(h_2)\big),$$

where h is the parameter of the surface which passes through the point.

Let the value of h which makes the surface (h, k) extend to infinity be denoted by h_∞; then putting $h_2=h_\infty$, we have $V_2=0$ (art. 7), and the last equation gives

$$V_1=\frac{4\pi dk}{n}\big(f(h_\infty)-f(h)\big);$$

and again, if this value of V_1 be substituted, the same equation gives

$$V_2=\frac{4\pi dk}{n}\big(f(h_\infty)-f(h_2)\big);$$

here V_1 is the potential of an infinitesimal shell on an *exterior* point, and V_2 on an *interior* point. These expressions suppose that the densities of the shells are $f'(h_1)$, $f'(h_2)$; hence, changing the densities to unity, and h_2 to h_1 in the second, we obtain the following results:—

The potential of the infinitesimal shell $\left(h_1, \frac{k+dk}{k}\right)$ (density $=1$) upon an *exterior* point is

$$\frac{4\pi dk}{nf'(h_1)}\big(f(h_\infty)-f(h)\big);$$

and upon an *interior* point, it is

$$\frac{4\pi dk}{nf'(h_1)}\big(f(h_\infty)-f(h_1)\big).$$

Now $f'(h)$ (art. 6) is $\frac{B}{\psi(}$; hence the above expressions become, for an *exterior* point,

$$\frac{4\pi}{n}\,dk\psi(h_1)\int_h^\infty\frac{dh}{\psi(h)}, \qquad \text{(E.)}$$

and for an *interior* point,

$$\frac{4\pi}{n}\,dk\psi(h_1)\int_{h_1}^\infty\frac{dh}{\psi(h)}. \qquad \text{(I.)}$$

9. In the expression (E.), the value of h at the lower limit of the integral is the parameter of the surface which passes through the attracted point, and the potential has therefore the same value at all points of that surface; hence

THEOREM V. *The external equipotential surfaces of the homogeneous infinitesimal shell* $\left(\mathrm{h}_1, \frac{\mathrm{k+dk}}{\mathrm{k}}\right)$ *are the surfaces* (h, k), *in which* h *is arbitrary and* k *invariable.*

The expression (I.) is independent of the position of the (interior) attracted point; hence

THEOREM VI. *The homogeneous infinitesimal shell* $\left(\mathrm{h}_1, \frac{\mathrm{k+dk}}{\mathrm{k}}\right)$ *exercises no force on an interior mass.* It follows evidently that the homogeneous finite shell $\left(h_1, \frac{k_2}{k_1}\right)$ possesses the same property.

10. The preceding articles contain all that is essential. But it may be as well to deduce the expression for the potential, on an exterior point, of the finite homogeneous shell $\left(h_1, \frac{k''}{k'}\right)$.

Let ξ, η, ζ be the coordinates of the attracted point. The expression (E.), art. 8, is a function of h, and through h a function of k; for h, at the lower limit of the integral, is a function of ξ, η, ζ, k, determined by the equation (art. 3)

$$f(\xi, \eta, \zeta, h, k)=0. \quad \ldots \ldots \ldots \quad (10.)$$

(I assume, for simplicity, that h_∞ is independent of k.) We have then to integrate (E.) with respect to k, from k' to k''. Now putting $F(h)$ for the integral in (E.), we have

$$\int F(h)dk = kF(h) - \int kF'(h)dh;$$

and, between the limits k', k'', this gives

$$\int_{k'}^{k''} F(h)dk = k''F(h'') - k'F(h') - \int_{h'}^{h''} kF'(h)dh;$$

where h'', h' are the values of h corresponding to k'', k', and given by the relation $f(\xi, \eta, \zeta, h, k)=0$. The actual value of $F(h)$ is $\int_h^{h_\infty} \frac{dh}{\psi(h)}$, and therefore $F'(h)=-\frac{1}{\psi(h)}$; hence the required potential is

$$\frac{4\pi}{n}\psi(h_1)\left\{k''\int_{h''}^{h_\infty}\frac{dh}{\psi(h)} - k'\int_{h'}^{h_\infty}\frac{dh}{\psi(h)} + \int_{h'}^{h''}\frac{kdh}{\psi(h)}\right\}, \quad \ldots \ldots \quad (P.)$$

where k, in the last integral, is the function of h determined by the equation (10.).

11. To verify this in the case of the ellipsoid, we have

$$\frac{x^2}{a^2+h}+\frac{y^2}{b^2+h}+\frac{z^2}{c^2+h}=k;$$

here $D^2k=2\left(\frac{1}{a^2+h}+\frac{1}{b^2+h}+\frac{1}{c^2+h}\right)=\varphi(h)$, and $Q_k^2+4\frac{dk}{dh}=0$, whence $n=4$; therefore

$$\psi(h)=\varepsilon^{\frac{1}{2}\int\varphi(h)dh}=\left((a^2+h)(b^2+h)(c^2+h)\right)^{\frac{1}{2}}*.$$

Also $h_\infty=\infty$. Let us take $k'=0$, $k''=1$, $h_1=0$, so that the formula (P.) will give the potential, on an external point (ξ, η, ζ), of the homogeneous solid ellipsoid

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{c^2}=1.$$

Then $\psi(h_1)=abc$; and h, k being now connected by the equation

$$\frac{\xi^2}{a^2+h}+\frac{\eta^2}{b^2+h}+\frac{\zeta^2}{c^2+h}=k,$$

we have $h'=\infty$, and $h''=$ the positive root of this equation when $k=1$. The expression (P.) then becomes

$$-\pi abc\int_{h''}^{\infty}\frac{\left(\frac{\xi^2}{a^2+h}+\frac{\eta^2}{b^2+h}+\frac{\zeta^2}{c^2+h}-1\right)dh}{\left((a^2+h)(b^2+h)(c^2+h)\right)^{\frac{1}{2}}},$$

which is the well-known value of the potential.

* The arbitrary constant, which might be introduced, would disappear in the result.

12. I shall conclude with an independent demonstration of the Theorem IV. art. 6.

Considering h as a function of x, y, z, k, by virtue of the equation $\mathrm{f}(x, y, z, h, k)=0$, we have

$$\mathrm{D}^2 f(h)=f''(h)\mathrm{Q}_h^2+f'(h)\mathrm{D}^2 h$$

($f(h)$ being any function of h, and the notation being that explained in art. 1).

Hence the condition of the possibility of satisfying the equation $\mathrm{D}^2 f(h)=0$, is that $\frac{\mathrm{D}^2 h}{\mathrm{Q}_h^2}$ be expressible as a function of h; if this be the case, $f(h)$ will be determined by the equation $\frac{f''(h)}{f'(h)}=-\frac{\mathrm{D}^2 h}{\mathrm{Q}_h^2}$. We have then to show that this condition will be fulfilled if the function $\mathrm{f}(x, y, z, h, k)$ be such that

$$\mathrm{D}^2 k=\phi(h), \quad \mathrm{Q}_k^2+n\frac{dk}{dh}=0.$$

It was proved in art. 3 that the latter of these equations gives

$$\mathrm{Q}_h.\mathrm{Q}_k=n,$$

and also that

$$\mathrm{Q}_k=-\frac{dk}{dh}\mathrm{Q}_h;$$

from which we obtain

$$\mathrm{Q}_h^2=-n\frac{dk}{dh}, \quad \mathrm{Q}_k^2=-n\left(\frac{dk}{dh}\right)^{-1} \quad \ldots\ldots\ldots \quad (11.)$$

Now suppose k expressed as a function of x, y, z, h; then considering h implicitly a function of x, y, z, k, we have, by two differentiations with respect to x,

$$0=\frac{dk}{dx}+\frac{dk}{dh}.\frac{dh}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12.)$$

$$0=\frac{d^2k}{dx^2}+2\frac{d^2k}{dhdx}.\frac{dh}{dx}+\frac{d^2k}{dh^2}\left(\frac{dh}{dx}\right)^2+\frac{dk}{dh}\frac{d^2h}{dx^2}.$$

Let the value of $\frac{dh}{dx}$ derived from (12.) be introduced in the last equation, and the similar results be written with respect to y and z; then we obtain by addition,

$$0=\mathrm{D}^2 k-2\left(\frac{dk}{dh}\right)^{-1}\Sigma\left(\frac{d^2k}{dhdx}.\frac{dk}{dx}\right)+\mathrm{Q}_h^2\frac{d^2k}{dh^2}+\frac{dk}{dh}\mathrm{D}^2 h \quad \ldots\ldots \quad (13.)$$

(using Σ to denote the sum of analogous expressions with respect to the three variables).

Now in the first of equations (11.), namely,

$$\left(\frac{dk}{dx}\right)^2+\left(\frac{dk}{dy}\right)^2+\left(\frac{dk}{dz}\right)^2=-n\frac{dk}{dh},$$

k is supposed to be expressed as a function of x, y, z, h, and the equation is therefore *identical*, for otherwise it would establish a relation between x, y, z, h, without k. Hence we may differentiate each side with respect to h; this gives

$$2\Sigma\left(\frac{dk}{dx}\frac{d^2k}{dhdx}\right)=-n\frac{d^2k}{dh^2}$$

$$=\mathrm{Q}_h^2\frac{dk}{dh}\frac{d^2k}{dh^2} \text{ (by (11.))};$$

hence the second and third terms of (13.) destroy one another; also $D^2k=\varphi(h)$, and $\frac{dk}{dh}=-\frac{n}{Q_h^2}$ by (11.); thus (13.) becomes, finally,

$$\varphi(h)-n\frac{D^2h}{Q_h^2}=0, \quad \text{or} \quad \frac{D^2h}{Q_h^2}=\frac{1}{n}\varphi(h).$$

It follows that the equation $D^2f(h)$ will be satisfied if $f(h)$ be determined by the equation

$$\frac{f''(h)}{f'(h)}=-\frac{1}{n}\varphi(h),$$

that is, if

$$f(h)=\int dh.\varepsilon^{-\frac{1}{n}\int\varphi(h)dh},$$

which is the theorem in question. This demonstration might have been given at the beginning of the investigation, and the theorem might have been made the foundation of the whole. But as there is nothing on the face of the assumed differential equations (5.), art. 3, to suggest the possibility of satisfying the condition $D^2f(h)=0$, the whole process would then have acquired the character of a *verification*, rather than of a demonstration following the natural order of discovery, in which latter form I wished it to appear.

II. *On an Extended Form of the Index Symbol in the Calculus of Operations.*

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Received November 24,—Read December 22, 1859.

IN the following paper I propose to resume more in detail the subject of a communication made to the Cambridge and Dublin Mathematical Journal (vol. viii. p. 25). The present investigations are restricted to the case of two variables.

§ 1. *The Theory of* ∇ *and* ∇_1.

Let

$$x\frac{d}{dx}+y\frac{d}{dy}=\nabla,$$

$$y\frac{d}{dx}+x\frac{d}{dy}=\nabla_1;$$

and let

$$x\frac{d'}{dx}+y\frac{d'}{dy}=\Xi,$$

$$y\frac{d'}{dx}+x\frac{d'}{dy}=\Xi_1,$$

where the accent indicates that in the combinations of Ξ, Ξ_1 the differentiations are to affect only the subject of operation, and not x or y, so far as they appear explicitly in the values of Ξ, Ξ_1. So that Ξ^2, $\Xi\,\Xi_1$, Ξ_1^2 are to be understood as follows:—

$$\Xi^2=x^2\frac{d^2}{dx^2}+2xy\frac{d^2}{dx\,dy}+y^2\frac{d^2}{dy^2},$$

$$\Xi\Xi_1=xy\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}\right)+(x^2+y^2)\frac{d^2}{dx\,dy},$$

$$\Xi_1^2=y^2\frac{d^2}{dx^2}+2yx\frac{d^2}{dx\,dy}+x^2\frac{d^2}{dy^2},$$

and so on for higher powers.

It will then be found that

$$\Xi^2=\nabla^2-\nabla\quad=(\nabla-1)\nabla,$$

$$\Xi\Xi_1=\nabla\nabla_1-\nabla_1=(\nabla-1)\nabla_1,$$

$$\Xi_1^2=\nabla_1^2-\nabla\quad=\nabla_1^2-\nabla.$$

Similarly,

$$\begin{aligned}
\Xi^2 &= \nabla\Xi^1 - 2\Xi^2 &&= (\nabla - 2)\Xi^2,\\
\Xi^2\Xi_1 &= \nabla\Xi\Xi_1 - 2\Xi\Xi_1 &&= (\nabla - 2)\Xi\Xi_1,\\
\Xi\,\Xi_1^2 &= \nabla\Xi_1^2 - 2\Xi_1^2 &&= (\nabla - 2)\Xi_1^2,\\
\Xi_1^2 &= \nabla_1\Xi_1^2 - 2\Xi\Xi_1 &&= \nabla\Xi_1^2 - 2\Xi\Xi_1.
\end{aligned}$$

And, generally,

$$\begin{aligned}
\Xi^n &= (\nabla - n + 1)\Xi^{n-1},\\
\Xi^{n-1}\Xi_1 &= (\nabla - n + 1)\Xi^{n-2}\Xi_1,\\
&\cdots\cdots\\
\Xi\Xi_1^{n-1} &= (\nabla - n + 1)\Xi_1^{n-1},\\
\Xi_1^n &= \nabla_1\Xi_1^{n-1} - (n-1)\Xi\Xi_1^{n-2}.
\end{aligned}$$

Before developing these expressions, the following formulæ deserve notice:—

$$\begin{aligned}
(\Xi \pm \Xi_1)^2 &= \nabla^2 \pm 2\nabla\nabla_1 + \nabla_1^2 - 2\nabla \mp 2\nabla_1\\
&= (\nabla \pm \nabla_1 - 2)(\nabla \pm \nabla_1).
\end{aligned}$$

Similarly, by arranging the terms of the third order thus,

$$\begin{aligned}
\Xi^3 &= \nabla\Xi^2 && && -2\Xi^3,\\
3\Xi^2\Xi_1 &= 2\nabla\Xi\Xi_1 + && \nabla_1\Xi^2 && -4\Xi\Xi_1 - 2\Xi\Xi_1,\\
3\Xi\,\Xi_1^2 &= && \nabla\Xi_1^2 && +2\nabla_1\Xi\Xi_1 - 2\Xi_1^2 - 2\Xi_1^2 - 2\Xi^3,\\
\Xi_1^3 &= && && \nabla_1\Xi_1^2 - 2\Xi\Xi_1,
\end{aligned}$$

we have

$$(\Xi \pm \Xi_1)^3 = (\nabla \pm \nabla_1 - 4)(\nabla \pm \nabla_1 - 2)(\nabla \pm \nabla_1).$$

And generally,

$$\begin{aligned}
\Xi^n &= && \nabla\Xi^{n-1} && && -(n-1) && \Xi^{n-1},\\
\tfrac{n}{1}\Xi^{n-1}\Xi_1 &= \tfrac{n-1}{1} && \nabla\Xi^{n-2}\Xi_1 + && \nabla_1\Xi^{n-1} && -(n-1)\tfrac{n-1}{1} && \Xi^{n-2}\Xi_1 - (n-1) && \Xi^{n-2}\Xi_1,\\
\tfrac{n(n-1)}{1.2}\Xi^{n-2}\Xi_1^2 &= \tfrac{(n-1)(n-2)}{1.2} && \nabla\Xi^{n-2}\Xi_1 + \tfrac{n-1}{1} && \nabla_1\Xi^{n-2}\Xi_1 - (n-1) && \tfrac{(n-1)(n-2)}{1.2} && \Xi^{n-3}\Xi_1^2 - \tfrac{(n-1)(n-2)}{1.2} && \Xi^{n-3}\Xi_1^2 - \tfrac{n-1}{1}\Xi^{n-1},
\end{aligned}$$

$$\cdots\cdots\cdots

So that, finally,

$$(\Xi\pm\Xi_1)^n=\{\nabla\pm\nabla_1-2(n-1)\}(\Xi\pm\Xi_1)^{n-1}$$
$$=\{\nabla\pm\nabla_1-2(n-1)\}\{\nabla\pm\nabla_1-2(n-2)\}..\{\nabla\pm\nabla_1-2\}\{\nabla\pm\nabla_1\},$$

the upper or the lower sign being taken throughout. And since

$$(\Xi\pm\Xi_1)^n=(x\pm y)^n\left(\frac{d}{dx}\pm\frac{d}{dy}\right)^n,$$

$$(x\pm y)^n\left(\frac{d}{dx}\pm\frac{d}{dy}\right)^n=\left\{(x\pm y)\left(\frac{d}{dx}\pm\frac{d}{dy}\right)-2(n-1)\right\}\left\{(x\pm y)\left(\frac{d}{dx}\pm\frac{d}{dy}\right)-2(n-2)\right\}..\left\{(x\pm y)\left(\frac{d}{dx}\pm\frac{d}{dy}\right)\right\},$$

an equation which might be established by other methods.

Returning to the expressions for $\Xi^r\Xi_1^s$, we have

$$\Xi^n=(\nabla-n+1)..(\nabla-2)(\nabla-1)\nabla,$$
$$\Xi^{n-1}\Xi_1=(\nabla-n+1)..(\nabla-2)(\nabla-1)\nabla_1,$$
$$\Xi^{n-2}\Xi_1^2=(\nabla-n+1)..(\nabla-2)(\nabla_1^2-\nabla),$$
$$\Xi^{n-3}\Xi_1^3=(\nabla-n+1)..(\nabla_1^3-3\nabla+2)\nabla_1,$$
$$\Xi^{n-4}\Xi_1^4=(\nabla-n+1)..(\nabla_1^4-6\nabla\nabla_1^2+3\nabla^2+8\nabla_1^2-6\nabla),$$
$$\Xi^{n-5}\Xi_1^5=(\nabla-n+1)..(\nabla_1^5-10\nabla_1^3\nabla+12\nabla_1^2-8\nabla_1^2\nabla+12\nabla_1\nabla^2+3\nabla^2-44\nabla_1\nabla-6\nabla_1^2+24\nabla_1),$$
$$\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot$$

These expressions are, however, determinants: thus,

$$\Xi^1=\begin{vmatrix}\nabla & 1\\ \nabla & \nabla\end{vmatrix}\qquad \Xi\Xi_1=\begin{vmatrix}\nabla & 1\\ \nabla_1 & \nabla_1\end{vmatrix}\qquad \Xi_1^2=\begin{vmatrix}\nabla_1 & 1\\ \nabla & \nabla_1\end{vmatrix}$$

$$\Xi^3=\begin{vmatrix}\nabla & 2 & .\\ \nabla & \nabla & 1\\ \nabla & \nabla & \nabla\end{vmatrix}\qquad \Xi^2\Xi_1=\begin{vmatrix}\nabla & 2 & .\\ \nabla & \nabla & 1\\ \nabla_1 & \nabla_1 & \nabla_1\end{vmatrix}\qquad \Xi\Xi_1^2=\begin{vmatrix}\nabla & 2 & .\\ \nabla_1 & \nabla_1 & 1\\ \nabla & \nabla & \nabla_1\end{vmatrix}\qquad \Xi_1^3=\begin{vmatrix}\nabla_1 & 2 & .\\ \nabla & \nabla_1 & 1\\ \nabla_1 & \nabla & \nabla_1\end{vmatrix}$$

The corresponding formulæ for $n=4$ are easily deduced from these, as follows:—For Ξ^4, $\Xi^3\Xi_1$, $\Xi^2\Xi_1^2$, $\Xi\Xi_1^3$, add to each determinant a row $(\nabla, 3, 0, 0)$, and a column having ∇ for its upper constituent, and for the remainder a repetition of the first column of the determinant to which it is added. For Ξ_1^4 the additional row is $(\nabla_1, 3, 0, 0)$, and the additional column ∇_1 with a repetition of the first column of $\Xi\Xi_1^3$. The formulæ then are

$$\Xi^4=\begin{vmatrix}\nabla & 3 & . & .\\ \nabla & \nabla & 2 & .\\ \nabla & \nabla & \nabla & 1\\ \nabla & \nabla & \nabla & \nabla\end{vmatrix}\qquad \Xi^3\Xi_1=\begin{vmatrix}\nabla & 3 & . & .\\ \nabla & \nabla & 2 & .\\ \nabla & \nabla & \nabla & 1\\ \nabla_1 & \nabla_1 & \nabla_1 & \nabla_1\end{vmatrix}\qquad \Xi^2\Xi_1^2=\begin{vmatrix}\nabla & 3 & . & .\\ \nabla & \nabla & 2 & .\\ \nabla_1 & \nabla_1 & \nabla_1 & 1\\ \nabla & \nabla & \nabla & \nabla_1\end{vmatrix}\qquad \Xi\Xi_1^3=\begin{vmatrix}\nabla & 3 & . & .\\ \nabla_1 & \nabla_1 & 2 & .\\ \nabla & \nabla & \nabla_1 & 1\\ \nabla_1 & \nabla_1 & \nabla & \nabla_1\end{vmatrix}\qquad \Xi_1^4=\begin{vmatrix}\nabla_1 & 3 & . & .\\ \nabla & \nabla_1 & 2 & .\\ \nabla_1 & \nabla & \nabla_1 & 1\\ \nabla & \nabla_1 & \nabla & \nabla_1\end{vmatrix}$$

And so also generally,

$$\Xi_1^i = \begin{vmatrix} \nabla_1 & i-1 & 0 & .. & 0 & 0 \\ \nabla & \nabla_1 & i-2 & .. & 0 & 0 \\ \nabla_1 & \nabla & \nabla_1 & .. & 0 & 0 \\ . & . & . & .. & . & . \\ \nabla_1 & \nabla & \nabla_1 & .. & \nabla_1 & 1 \\ \nabla & \nabla_1 & \nabla & .. & \nabla & \nabla_1 \end{vmatrix}, \text{ or } = \begin{vmatrix} \nabla_1 & i-1 & 0 & .. & 0 & 0 \\ \nabla & \nabla_1 & i-2 & .. & 0 & 0 \\ \nabla_1 & \nabla & \nabla_1 & .. & 0 & 0 \\ . & . & . & .. & . & . \\ \nabla & \nabla_1 & \nabla & .. & \nabla_1 & 1 \\ \nabla_1 & \nabla & \nabla_1 & .. & \nabla & \nabla_1 \end{vmatrix}$$

according as i is even or odd. And the expression for Ξ^i/Ξ_1^i is to be formed from this by adding the following j rows (each consisting of $(i+j)$ places), viz.

$$\begin{matrix} \nabla & i+j-1 & 0 & .. & 0 & 0 \\ \nabla & \nabla & i+j-2 & .. & 0 & 0 \\ . & . & . & .. & . & . \\ \nabla & \nabla & \nabla & .. & 0 & 0 \end{matrix}$$

and repeating the first column of Ξ_1^i j times, so as to complete the square.

By means of these formulæ the expression

$$a\Xi^n + \tfrac{n}{1} b\Xi^{n-1}\Xi_1 + .. = (a, b, .. \text{)(}\Xi, \Xi_1)^n$$

may be exhibited as a function of ∇, ∇_1.

There is, however, another way in which this transformation may be effected. Let $\alpha, \beta\,;\ \alpha_1, \beta_1\,; ..$ be the roots of the equation

$$(a, b, .. \text{)(}\Xi, \Xi_1)^n = 0$$

solved with respect to $\Xi : \Xi_1$. Then

$$\begin{aligned} &(a, b, c\text{)(}\Xi, \Xi_1)^2 = (\alpha_1\Xi + \beta_1\Xi_1)(\alpha\Xi + \beta\Xi_1) \\ &= (\nabla\nabla_1\text{)(}\alpha_1\beta_1)(\alpha\Xi + \beta\Xi_1) - \alpha_1(\alpha\Xi + \beta\Xi_1) - \beta_1(\alpha\Xi_1 + \beta\Xi) \\ &= (\nabla\nabla_1\text{)(}\alpha_1\beta_1)(\nabla\nabla_1\text{)(}\alpha\beta) - (\nabla\nabla_1\nabla\text{)(}\alpha_1\beta_1\text{)(}\alpha\beta). \end{aligned}$$

Similarly,

$$\begin{aligned} &(a\,b\,c\,d\text{)(}\Xi\Xi_1)^3 \\ &= (\alpha_2\Xi + \beta_2\Xi_1)(\alpha_1\Xi + \beta_1\Xi_1)(\alpha\Xi + \beta\Xi) \\ &= (\alpha_2\nabla + \beta_2\nabla_1)(\alpha_1\Xi + \beta_1\Xi_1)(\alpha\Xi + \beta\Xi_1) \\ &\quad - 2\alpha_2\ (\alpha_1\Xi + \beta_1\Xi_1)(\alpha\,\Xi + \beta\Xi_1) \\ &\quad - \beta_2\ (\alpha_1\Xi_1 + \beta_1\Xi)(\alpha\,\Xi + \beta\Xi_1) \\ &\quad - \beta_2\ (\alpha_1\Xi + \beta_1\Xi_1)(\alpha\,\Xi_1 + \beta\Xi) \end{aligned}$$

$$
\begin{aligned}
&=(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1(\alpha\beta)-(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1\nabla(\alpha_1\beta_1(\alpha\beta)\\
&\quad-2\alpha_3(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1(\alpha\beta)+2\alpha_3(\nabla\nabla_1\nabla(\alpha_1\beta_1(\alpha\beta)\\
&\quad-\beta_3(\nabla\nabla_1(\beta_1\alpha_1)(\nabla\nabla_1(\alpha\beta)+\beta_3(\nabla_1\nabla\nabla_1(\alpha_1\beta_1(\alpha\beta)\\
&\quad-\beta_3(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1(\beta\alpha)+\beta_3(\nabla_1\nabla\nabla_1(\alpha_1\beta_1(\alpha\beta)\\
&=(\nabla\nabla(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1(\alpha\beta)\\
&\quad-(\nabla\nabla_1(\alpha\beta)(\nabla\nabla_1\nabla(\alpha_1\beta_1(\alpha_2\beta_3)\\
&\quad-(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha\beta)\\
&\quad-(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1\nabla(\alpha\beta(\alpha_1\beta_1)\\
&\quad+2(\nabla\nabla_1\nabla\nabla_1(\alpha_2\beta_3(\alpha_1\beta_1(\alpha\beta).
\end{aligned}
$$

The expanded form of this is

$$
\begin{aligned}
&(\alpha_2\nabla+\beta_2\nabla_1)(\alpha_1\nabla+\beta_1\nabla_1)(\alpha\nabla+\beta\nabla_1)\\
&-(\alpha\nabla+\beta\nabla_1)\{(\alpha_1\alpha_2+\beta_1\beta_2)\nabla+(\alpha_1\beta_2+\alpha_2\beta_1)\nabla_1\}\\
&-(\alpha_1\nabla+\beta_1\nabla_1)\{(\alpha_2\alpha+\beta_2\beta)\nabla+(\alpha_2\beta+\alpha\beta_2)\nabla_1\}\\
&-(\alpha_2\nabla+\beta_2\nabla_1)\{(\alpha\alpha_1+\beta\beta_1)\nabla+(\alpha\beta_1+\alpha_1\beta)\nabla_1\}\\
&\quad+2\{(\alpha\alpha_1\alpha_2+\alpha\beta_1\beta_2+\alpha_1\beta_2\beta+\alpha_2\beta\beta_1)\nabla\\
&\qquad+(\beta\beta_1\beta_2+\beta\alpha_1\alpha_2+\beta_1\alpha_2\alpha+\beta_2\alpha\alpha_1)\nabla_1\}\\
&=a\nabla^3+3b\nabla^2\nabla_1+3c\nabla\nabla_1^2+d\nabla_1^3\\
&\quad-3(a+c)\nabla^2-3(3b+d)\nabla\nabla_1-bc\nabla_1^2\\
&\qquad+2(a+3c)\nabla+2(3b+d)\nabla_1.
\end{aligned}
$$

To these may be added,

$$
\begin{aligned}
&(a\ b\ c\ d\ e(\Xi\ \Xi_1)^4\\
&=(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1(\alpha\beta)\\
&\quad-(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha\beta)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha_1\beta_1)\\
&\quad-(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha\beta)\\
&\quad-(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1\nabla(\alpha_1\beta_1(\alpha\beta)\\
&\quad-(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha\beta)\\
&\quad-(\nabla\nabla_1(\alpha\beta)(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha_1\beta_1)\\
&\quad-(\nabla\nabla_1(\alpha_1\beta_1)(\nabla\nabla_1(\alpha\beta)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha_2\beta_3)\\
&\qquad+2(\nabla\nabla_1(\alpha\beta)(\nabla\nabla_1\nabla\nabla_1(\alpha_2\beta_3(\alpha_2\beta_3(\alpha_1\beta_1)\\
&\qquad+2(\nabla\nabla_1(\alpha_2\beta_1)(\nabla\nabla_1\nabla\nabla_1(\alpha\beta(\alpha_2\beta_3(\alpha_2\beta_3)\\
&\qquad+2(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1\nabla\nabla_1(\alpha_1\beta_1(\alpha\beta(\alpha_2\beta_3)\\
&\qquad+2(\nabla\nabla_1(\alpha_2\beta_3)(\nabla\nabla_1\nabla\nabla_1(\alpha_2\beta_3(\alpha_1\beta_1(\alpha\beta)\\
&\qquad+(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha\beta)(\nabla\nabla_1\nabla(\alpha_2\beta_3(\alpha_1\beta_1)
\end{aligned}
$$

$$
\begin{aligned}
&+(\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_1\beta_1)(\nabla\nabla_1\nabla)(\alpha\,\beta)(\alpha_2\beta_2)\\
&+(\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_2\beta_2)(\nabla\nabla_1\nabla)(\alpha_1\beta_1)(\alpha\,\beta)\\
&-6(\nabla\nabla_1\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_2\beta_2)(\alpha_1\beta_1)(\alpha\beta)\\
&=a\nabla^4+4b\nabla^3\nabla_1+6c\nabla^2\nabla_1^2+4d\nabla\nabla_1^3+e\nabla_1^4\\
&-6\{(a+c)\nabla^3+2(2b+d)\nabla^2\nabla_1+(5c+e)\nabla\nabla_1^2+2d\nabla_1^3\}\\
&+(11a+30c+3d)\nabla^2+44(b+d)\nabla\nabla_1+4(6c+2d+3e)\nabla_1^2\\
&\quad-6\{(a+6c+e)\nabla+4(b+d)\nabla_1\}.
\end{aligned}
$$

There is considerable resemblance between these functions and determinants; and although the factors of which the various terms are composed do not admit of being arranged as constituents of the determinants which they resemble, yet a symbolical notation will render such an arrangement possible. For this purpose, let $(\nabla\nabla_i)(\alpha_i\beta_i)$ and $(\alpha_j\beta_j)$ be the symbolical factors of $(\nabla\nabla_i\nabla)(\alpha_i\beta_i)(\alpha_j\beta_j)$; so that

$$(\nabla\nabla_1)(\alpha_2\beta_2)\times(\alpha_1\beta_1)=(\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_1\beta_1)$$

$$(\nabla\nabla_1)(\alpha_2\beta_2)\times(\alpha_1\beta_1)\times(\alpha\beta)=(\nabla\nabla_1\nabla\nabla_1)(\alpha_2\beta_2)(\alpha_1\beta_1)(\alpha\beta),$$

and so on. Then

$$
\begin{aligned}
&(a\,b\,c)(\Xi\Xi_1)^3\\
&=\begin{vmatrix}(\nabla\nabla_1)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_1\beta_1) & (\nabla\nabla_1)(\alpha\beta)\end{vmatrix}\\
&(a\,b\,c)(\Xi\Xi_1)^3\\
&=\begin{vmatrix}(\nabla\nabla_1)(\alpha_2\beta_2) & (\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\nabla\nabla_1)(\alpha\beta)\end{vmatrix}
\end{aligned}
$$

By means of these formulæ, the corresponding expressions for higher degrees may be established. Thus, for the fourth degree,

$$
\begin{aligned}
&(a\,b\,c\,d\,e)(\Xi\,\Xi_1)^4\\
&=(\alpha_3\Xi+\beta_3\Xi_1)(\alpha_2\Xi+\beta_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\alpha\Xi+\beta\Xi)\\
&=(\alpha_3\nabla+\beta_3\nabla_1)(\alpha_2\Xi+\beta_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-3\alpha_3(\alpha_2\Xi+\beta_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-\beta_3(\beta_2\Xi+\alpha_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-\beta_3(\beta_2\Xi+\beta_2\Xi_1)(\beta_1\Xi+\alpha_1\Xi_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-\beta_3(\alpha_2\Xi+\beta_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\beta\Xi+\alpha\Xi_1)\\
&=(\alpha_3\nabla+\beta_3\nabla_1)(\alpha_2\Xi+\beta_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-(\Xi\Xi_1\Xi)(\alpha_2\beta_2)(\alpha_2\beta_2)(\alpha_1\Xi+\beta_1\Xi_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-(\alpha_2\Xi+\beta_2\Xi_1)(\Xi\Xi_1\Xi)(\alpha_2\beta_2)(\alpha_1\beta_1)(\alpha\Xi+\beta\Xi_1)\\
&\quad-(\alpha_2\Xi+\beta_2\Xi_1)(\alpha_1\Xi+\beta_1\Xi_1)(\Xi\Xi\;\Xi)(\alpha_2\beta_2)(\alpha\beta)
\end{aligned}
$$

$$=(\nabla\nabla_1)(\alpha_2\beta_2)\begin{vmatrix}(\nabla\nabla_1)(\alpha_2\beta_2) & (\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\nabla\nabla_1)(\alpha\beta)\end{vmatrix}$$

$$-\begin{vmatrix}(\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_2\beta_2) & (\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\nabla\nabla_1)(\alpha\beta)\end{vmatrix}$$

$$-\begin{vmatrix}(\nabla\nabla_1)(\alpha_2\beta_2) & (\alpha_2\beta_2)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha_1\beta_1) & (\nabla\nabla_1)(\alpha\beta)\end{vmatrix}$$

$$-\begin{vmatrix}(\nabla\nabla_1)(\alpha_2\beta_2) & (\alpha_1\beta_1) & (\alpha_2\beta_2)(\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\alpha_2\beta_2)(\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\nabla\nabla_1\nabla)(\alpha_2\beta_2)(\alpha\beta)\end{vmatrix}$$

Transposing the columns of the third of these determinants, the sign becomes changed, and the sum

$$=\begin{vmatrix}(\nabla\nabla_1)(\alpha_2\beta_2) & (\alpha_2\beta_2) & (\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_2\beta_2) & (\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\alpha\beta)\\ (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_2\beta_2) & (\nabla\nabla_1)(\alpha_1\beta_1) & (\nabla\nabla_1)(\alpha\beta)\end{vmatrix}$$

And as the above process is perfectly general in principle, we may conclude the general expression

$$(a\,b\,..)(\Xi\Xi_1)^n$$
$$=\begin{vmatrix}(\nabla\nabla_1)(\alpha_n\beta_n) & (\alpha_{n-1}\beta_{n-1}) & .. & (\alpha_1\beta_1)\\ (\nabla\nabla_1)(\alpha_n\beta_n) & (\nabla\nabla_1)(\alpha_{n-1}\beta_{n-1}) & .. & (\alpha_1\beta_1)\\ \cdot & \cdot & .. & \cdot\\ (\nabla\nabla_1)(\alpha_n\beta_n) & (\nabla\nabla_1)(\alpha_{n-1}\beta_{n-1}) & .. & (\nabla\nabla_1)(\alpha_1\beta_1)\end{vmatrix}$$

In order to alculate the effect of the operation ∇_1, and so that of the operation $(a\,b\,..)(\Xi\,\Xi_1)^n$ upon a given function, let

$$u=a_0x^n+a_1x^{n-1}y+..$$
$$=\Sigma a_ix^{n-i}y^i.$$

Then

$$\nabla_1u=\Sigma a_i\{(n-i)x^{n-i-1}y^{i+1}+ix^{n-i+1}y^{i-1}\}$$
$$=\Sigma\{(n-i+1)a_{i-1}+(i+1)a_{i+1}\}x^{n-i}y^i.$$

Now

$$\epsilon^{k\frac{d}{d\theta}}f(\theta)=f(\theta+k).$$

Hence

$$\nabla_1 u = \Sigma\left\{(n-i+1)\varepsilon^{-\frac{d}{dx}} + (i+1)\varepsilon^{\frac{d}{dx}}\right\} a_i x^{n-i} y^i,$$

$$\nabla_1^2 u = \Sigma\left\{(n-i+1)\varepsilon^{-\frac{d}{dx}} + (i+1)\varepsilon^{\frac{d}{dx}}\right\}^2 a_i x^{n-i} y^i,$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\nabla_1^m u = \Sigma\left\{(n-i+1)\varepsilon^{-\frac{d}{dx}} + (i+1)\varepsilon^{\frac{d}{dx}}\right\}^m a_i x^{n-i} y^i,$$

where the operative factor must be understood to affect the suffixes of the as and the is in the coefficients, and not the indices of the variables. In the use of these formulæ, however, it is to be observed that the order of the multiplications must be retained. Thus:

$$\begin{aligned}
&\left\{(n-i+1)\varepsilon^{-\frac{d}{dx}} + (i+1)\varepsilon^{\frac{d}{dx}}\right\}^2 a_i \\
&= \left\{(n-i+1)\varepsilon^{-\frac{d}{dx}}(n-i+1)\varepsilon^{-\frac{d}{dx}}\right. \\
&\quad + (n-i+1)\varepsilon^{-\frac{d}{dx}}(i+1)\varepsilon^{\frac{d}{dx}} \\
&\quad + \quad (i+1)\varepsilon^{\frac{d}{dx}}(n-i+1)\varepsilon^{-\frac{d}{dx}} \\
&\quad + \quad \left.(i+1)\varepsilon^{\frac{d}{dx}}(i+1)\varepsilon^{\frac{d}{dx}}\right\} a_i \\
&= \left\{(n-i+1)(n-i+2)\varepsilon^{-2\frac{d}{dx}} + (n-i+1)i + (n-i)(i+1) + (i+1)(i+2)\varepsilon^{2\frac{d}{dx}}\right\} a_i \\
&= (n-i+1)(n-i+2)a_{i-2} + \left\{(n-i+1)i + (n-i)(i+1)\right\} a_i + (i+1)(i+2)a_{i-2}.
\end{aligned}$$

Similarly, since

$$\begin{aligned}
(a+b)^3 = {} & a\,a\,a \\
& + b\,a\,a \\
& + a\,b\,a \\
& + a\,a\,b \\
& + a\,b\,b \\
& + b\,a\,b \\
& + b\,b\,a \\
& + b\,b\,b.
\end{aligned}$$

Therefore

$$\begin{aligned}
&\left\{(n-i+1)\varepsilon^{-\frac{d}{dx}} + (i+1)\varepsilon^{\frac{d}{dx}}\right\}^3 a_i \\
&= \left[(n-i+1)(n-i+2)(n-i+3)\varepsilon^{-3\frac{d}{dx}}\right. \\
&\quad + \left\{(i+1)(n-i)(n-i+1) + (n-i+1)i(n-i+1) + (n-i+1)(n-i+2)(i-1)\right\}\varepsilon^{-\frac{d}{dx}} \\
&\quad + \left\{(n-i+1)i(i+1) + (i+1)(n-i)(i+1) + (i+1)(i+2)(n-i-1)\right\}\varepsilon^{\frac{d}{dx}} \\
&\quad + \quad \left.(i+1)(i+2)(i+3)\varepsilon^{3\frac{d}{dx}}\right] a_i
\end{aligned}$$

$$= (n-i+1)(n-i+2)(n-i+3)a_{i-3}$$
$$+\{(n-i)(n-i+1)(i+1)+(n-i+1)^2 i+(n-i+1)(n-i+2)(i-1)\}a_{i-1}$$
$$+\{(n-i+1)i(i+1)+(n-i)(i+1)^2+(n-i-1)(i+1)(i+2)\}a_{i+1}$$
$$+ (i+1)(i+2)(i+3)a_{i+3},$$

and so on for higher degrees.

But it is also required to determine the effect of negative powers of ∇_1 on a given function. For this purpose let

$$U=\Sigma A_r x^{n-i}y^i$$

and

$$\nabla_1^{-1}U=u, \text{ or } U=\nabla_1 u.$$

Then equating coefficients,

$$\begin{aligned} 1a_1 &= A_0, \\ na_0 + 2a_2 &= A_1, \\ (n-1)a_0 + 3a_3 &= A_2, \\ \cdots\cdots\cdots\cdots & \\ 3a_{n-2}+(n-1)a_{n-1} &= A_{n-2}, \\ 2a_{n-2}+ na_n &= A_{n-1}, \\ a_{n-1} &= A_n; \end{aligned}$$

whence, by actual elimination,

$$a_1=\frac{1}{1}A_0,$$

$$a_2=\frac{1}{2}A_2-\frac{n-1}{2}a_1$$
$$=\frac{1}{2}\left(A_2-\frac{n-1}{1}A_0\right),$$

$$a_3=\frac{1}{3}\left(A_3-(n-3)a_2\right)$$
$$=\frac{1}{3}\left(A_3-\frac{n-3}{2}A_2+\frac{(n-3)(n-1)}{2.1}A_0\right),$$

$$a_4=\frac{1}{4}\left(A_4-(n-5)a_3\right)$$
$$=\frac{1}{4}\left(A_4-\frac{n-5}{3}A_3+\frac{(n-5)(n-3)}{3.2}A_2-\frac{(n-5)(n-3)(n-1)}{3.2.1}A_0\right),$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$a_{2m+1}=\frac{1}{2m+1}\left(A_{2m}-\frac{n-2m+1}{2m-1}A_{2m-2}+\frac{(n-2m+1)(n-2m+3)}{(2m-1)(2m-3)}A_{2m-4}-\cdots\right.$$
$$\left.(-)^m\frac{(n-2m+1)(n-2m+3)\cdots(n-1)}{(2m-1)(2m-3)\cdots1}A_0\right);$$

and for the even indices,

$$a_2=\frac{1}{2}\left(A_1-na_0\right),$$

$$a_4=\frac{1}{4}\left(A_3-(n-2)a_2\right)$$

$$=\frac{1}{4}\left(A_3-\frac{n-2}{2}A_1+\frac{(n-2)n}{2.1}a_0\right),$$

$$a_6=\frac{1}{6}\left(A_5-(n-4)a_4\right)$$

$$=\frac{1}{6}\left(A_5-\frac{n-4}{4}A_3+\frac{(n-4)(n-2)}{4.2}A_1-\frac{(n-4)(n-2)n}{4.2.1}a_0\right),$$

. . . . . .

But it is better to make use of the operative symbol for the solution of the equations; thus:

$$(n-i+2)a_{i-2}+ia_i=A_{i-1}$$

$$\left\{(n-i+2)\epsilon^{-2\frac{d}{di}}+i\right\}a_i=A_{i-1}, \text{ or } \left\{(n-i+2)\epsilon^{-2\frac{d}{di}}\frac{1}{i}+1\right\}ia_i=A_{i-1};$$

whence

$$a_i=\left\{(n-i+2)\epsilon^{-2\frac{d}{di}}\frac{1}{i}+\right\}^{-1}A_{i-1},$$

$$a_i=\frac{1}{i}\left\{1+(n-i+2)\epsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^{-1}A_{i-1},$$

$$a_i=\frac{1}{i}\left\{A_{i-1}-\frac{n-i+2}{i-2}A_{i-3}+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}A_{i-5}-..\right\};$$

the last term being

$$(-)^{\frac{i-1}{2}}\frac{(n-i+2)(n-i+4)..(n-1)}{(i-2)(i-4)..1}A_0 \text{ when } i \text{ is odd,}$$

and

$$(-)^{\frac{i}{2}}\frac{(n-i+2)(n-i+4)..n}{(i-2)(i-4)..2}a_0 \text{ when } i \text{ is even.}$$

The two cases, however, of n even and n odd require special notice. If n be odd, the last equation of the series for determining the as may be thus written:

$$na_{n+1}=0=A_n-\frac{1}{n-1}A_{n-2}+\frac{1.3}{(n-1)(n-3)}A_{n-4}-..(-)^{\frac{n+1}{2}}\frac{1.3..n}{(n-1)(n-3)..2}a_0,$$

which determines a_0.

But in the case of n being even,

$$na_{n+1}=0=A_n-\frac{1}{n-1}A_{n-2}+\frac{1.3}{(n-1)(n-3)}A_{n-4}-..(-)^{\frac{n}{2}}A_0;$$

a relation between the As alone. The explanation of this apparent anomaly is to be sought in the complementary arbitrary function arising out of the operation $\nabla_i^{-1}0$.

In the case of $\nabla_1^2 u$,

$$a_i = \left\{(n-i+2)\varepsilon^{-2\frac{d}{di}}+i\right\}^2 \mathrm{A}_{i-1}$$

$$= \frac{1}{i}\left\{1+(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^{-1}\frac{1}{i}\left\{1+(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^{-1}\mathrm{A}_{i-1}$$

$$= \frac{1}{i}\left\{1+(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^{-1}\frac{1}{i}\left\{\mathrm{A}_{i-1}-\frac{n-i+2}{i-2}\mathrm{A}_{i-3}+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\mathrm{A}_{i-5}-\ldots\right\}$$

$$= \frac{1}{i}\left\{1-\left\{(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}+\left\{(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^2-\ldots\right\}\frac{1}{i}\left\{\mathrm{A}_{i-1}-\frac{n-i+2}{i-2}\mathrm{A}_{i-3}+\ldots\right\}.$$

But

$$\left\{(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^2 = (n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\frac{n-i+2}{i-2}\varepsilon^{-2\frac{d}{di}}$$

$$= \frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\varepsilon^{-4\frac{d}{di}},$$

$$\left\{(n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\right\}^3 = (n-i+2)\varepsilon^{-2\frac{d}{di}}\frac{1}{i}\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\varepsilon^{-4\frac{d}{di}}$$

$$= \frac{(n-i+2)(n-i+4)(n-i+6)}{(i-2)(i-4)(i-6)}\varepsilon^{-6\frac{d}{di}}.$$

Therefore

$$ia_i = \frac{1}{i}\left\{\mathrm{A}_{i-1}-\frac{n-i+2}{i-2}\mathrm{A}_{i-3}+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\mathrm{A}_{i-5}-\ldots\right\}$$

$$-\frac{1}{i-2}\left\{\frac{n-i+2}{i-2}\mathrm{A}_{i-3}-\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\mathrm{A}_{i-5}+\ldots\right\}$$

$$+\frac{1}{i-4}\left\{\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\mathrm{A}_{i-5}-\ldots\right\}$$

$$-\qquad\qquad\ldots\Big\}$$

$$= \frac{1}{i}\mathrm{A}_{i-1}$$

$$-\left(\frac{1}{i}+\frac{1}{i-2}\right)\frac{n-i+2}{i-2}\mathrm{A}_{i-3}$$

$$+\left(\frac{1}{i}+\frac{1}{i-2}+\frac{1}{i-4}\right)\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\mathrm{A}_{i-5}$$

$$-\ldots,$$

the last term being

$$(-)^{\frac{i-1}{2}}\left(\frac{1}{i}+\frac{1}{i-2}+\ldots+\frac{1}{3}+1\right)\frac{(n-i+2)(n-i+4)\ldots(n-1)}{(i-2)(i-4)\ldots 1}\mathrm{A}_0 \text{ when } i \text{ is odd,}$$

and

$$(-)^{\frac{i}{2}}\left(\frac{1}{i}+\frac{1}{i-2}+\ldots+\frac{1}{4}+\frac{1}{2}\right)\frac{(n-i+2)(n-i+4)\ldots n}{(i-2)(i-4)\ldots 2}a_0 \text{ when } i \text{ is even.}$$

For $\nabla_1^s u$,

$$ia_i=\left\{1-\frac{n-i+2}{i-2}\epsilon^{-2\frac{d}{dx}}+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\epsilon^{-4\frac{d}{dx}}-..\right\}\frac{1}{i}\left\{\frac{1}{i}A_{i-1}-\left(\frac{1}{i}+\frac{1}{i-2}\right)\frac{n-i+2}{i-2}A_{i-3}+..\right\}$$

$$=\frac{1}{i}\left\{\frac{1}{i}A_{i-1}-\left(\frac{1}{i}+\frac{1}{i-2}\right)\frac{n-i+2}{i-2}A_{i-3}+..\right\}$$

$$-\frac{n-i+2}{i-2}\cdot\frac{1}{(i-2)}\left\{\frac{1}{i-2}A_{i-3}-\left(\frac{1}{i-2}+\frac{1}{i-4}\right)\frac{n-i+4}{i-4}A_{i-5}+..\right\}$$

$$+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\frac{1}{i-4}\left\{\frac{1}{i-4}A_{i-5}-\left(\frac{1}{i-4}+\frac{1}{i-6}\right)\frac{n-i+6}{i-6}A_{i-7}+..\right\}$$

$$-\ldots$$

and writing for convenience $\left(\frac{1}{i},\frac{1}{i-2}..\right)^m=\left(\frac{1}{i}\right)^m+\left(\frac{1}{i}\right)^{m-1}\frac{1}{i-2}+..$, *i. e.* the multinomial expansion with the numerical coefficients suppressed,

$$ia_i=\left(\frac{1}{i}\right)^2A_{i-1}$$

$$-\frac{n-i+2}{i-2}\left(\frac{1}{i},\frac{1}{i-2}\right)^2A_{i-3}$$

$$+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\left(\frac{1}{i},\frac{1}{i-2},\frac{1}{i-4}\right)^2A_{i-5}$$

$$-\ldots$$

the last term being

$$(-)^{\frac{i-1}{2}}\frac{(n-i+2)(n-i+4)..(n-1)}{(i-2)(i-4)..1}\left(\frac{1}{i},\frac{1}{i-2},..\frac{1}{3},1\right)^2A_0 \text{ when } i \text{ is odd,}$$

and

$$(-)^{\frac{i}{2}}\frac{(n-i+2)(n-i+4)..n}{(i-2)(i-4)..2}\qquad\left(\frac{1}{i},\frac{1}{i-2},..\frac{1}{3},1\right)^2a_0 \text{ when } i \text{ is even.}$$

And from the way in which the coefficients are formed, it is easy to see that in the case of $\nabla_1^m u$,

$$ia_i=\left(\frac{1}{i}\right)^{m-1}A_{i-1}$$

$$-\frac{n-i+2}{i-2}\left(\frac{1}{i},\frac{1}{i-2}\right)^mA_{i-3}$$

$$+\frac{(n-i+2)(n-i+4)}{(i-2)(i-4)}\left(\frac{1}{i},\frac{1}{i-2},\frac{1}{i-4}\right)^mA_{i-5}$$

$$-\ldots$$

with conditions for i even and i odd, similar to those given in the cases of ∇_1^2, ∇_1^3,

And since it has been shown above that

$$F(\nabla_1)u=\Sigma\left\{F\left((n-i+1)\epsilon^{-\frac{d}{dx}}+(i+1)\epsilon^{\frac{d}{dx}}\right)\right\}a_ix^{n-i}y$$

it follows that, if

$$\left\{F(\nabla_1)\right\}^{-1}U=u,$$

the coefficients of u will be given by the equation

$$a_i=\left\{F\left((n-i+1)\varepsilon^{-\frac{d}{di}}+(i+1)\varepsilon^{\frac{d}{di}}\right)\right\}^{-1}A_i.$$

Still more generally,

$$F(\nabla,\nabla_1)u=\Sigma\left\{F\left(n,(n-i+1)\varepsilon^{-\frac{d}{di}}+(i+1)\varepsilon^{\frac{d}{di}}\right)\right\}a_ix^{n-i}y.$$

So that the effect of the operation

$$(a\,b\,..\,\chi\Xi\,\Xi_1)^n,$$

or, as it may also be written,

$$(a\,b\,..\,\chi xy)^n\frac{d^n}{dx^n}+\frac{n}{1}(a\,b\,..\,\chi xy^{n-1}\chi yx)\frac{d^n}{dx^{n-1}dy}+..,$$

will be exhibited by replacing ∇, ∇_1 by n, and $(n-i+1)\varepsilon^{-\frac{d}{di}}+(i+1)\varepsilon^{\frac{d}{di}}$ respectively in either of the values given for $(ab\,..\,\chi\Xi\,\Xi_1)^n$ in pages 16 or 19.

In order, therefore, to solve the differential equation

$$(a\,b\,..\,\chi\Xi\,\Xi_1)^nu=0,$$

we must first reduce it to the form

$$F(\nabla\,\nabla_1)u=0;$$

then solving the symbolical equation

$$K^{-1}F(\nabla\,\nabla_1)=0$$

(where K is the coefficient of the highest power of ∇_1) with respect to ∇_1, and calling the roots $f_1(\nabla), f_2(\nabla), ..f_m(\nabla)$, or simply $f_1, f_2, ..f_m$, we have

$$u=\frac{0}{F(\nabla,\nabla_1)}=\frac{0}{K(\nabla_1-f_1)(\nabla_1-f_2)..(\nabla_1-f_m)}$$

$$=\frac{1}{K}\left(\frac{C_1}{\nabla_1-f_1}+\frac{C_2}{\nabla_1-f_2}+..\frac{C_m}{\nabla_1-f_m}\right)0,$$

where

$$C_1=\frac{f_1^{m-1}}{(f_1-f_2)(f_1-f_3)..(f_1-f_m)},\quad C_2=\frac{f_2^{m-1}}{(f_2-f_1)(f_2-f_3)..(f_2-f_m)},..$$

In order to evaluate the expression for u, let $p_1, p_2, ..p_m$ be values of ∇ which make $f_1, f_2, ..f_m$ vanish. They may in fact be called roots of $f_1, f_2, ..f_m$; but as these functions are generally irrational, they cannot be replaced by the products of factors of the form $\nabla-p$. In general there will be only one quantity p for each function f; because if f be rationalized, it will give rise to a function of the degree m; but although the equation so formed will in general have m roots, $(m-1)$ of them will in fact be extraneous to the particular equation rationalized, and belong one apiece to each of the remaining equations of the system.

Let, then, $u_{p_1}, u_{p_2}, \ldots u_{p_m}$ be arbitrary homogeneous functions of x, y, of the degrees p_1, $p_2, \ldots p_m$ respectively; then, since

$$f(\nabla)u_p = f(p)u_p = 0, \text{ because } f(p) = 0,$$

we may make

$$\frac{0}{f(\nabla)} = u_p,$$

and consequently

$$u = \frac{1}{K}\Sigma\frac{C_i}{\nabla_1 - f_i}0 = -\frac{1}{K}\Sigma\frac{C_i}{1-\frac{\nabla_1}{f_i}}\cdot\frac{0}{f_i} = -\frac{1}{K}\Sigma\frac{C_i}{1-\frac{\nabla_1}{f_i}}u$$

or replacing C_i by its value,

$$u = -\frac{1}{K}\Sigma\frac{f_i^m}{(f_i-f_1)(f_i-f_2)}\cdots\frac{1}{f_i-\nabla_1}u_{p_i}$$

$$= \frac{1}{K}\Sigma\frac{f_i(p_i)^m}{\big(f_i(p_i)-f_1(p_i)\big)\big(f_i(p_i)-f_2(p_i)\big)}\cdots\frac{1}{\nabla_1-f_i(p_i)}u_{p_i}.$$

This expression, however, leads only to illusory results, for $f_i(p_i)=0$; and consequently on developing $\frac{1}{\nabla_1 - f_i(p_i)}$, even in descending powers of $f_i(p_i)$, the first m terms vanish, and all the terms after the $(m+1)$th become infinite; the $(m+1)$th alone being finite.

The following method is, however, free from this difficulty. Select any second suffix j; then

$$u = -\frac{1}{K}\Sigma\frac{C_i}{f_i-\nabla_1}0$$

$$= -\frac{1}{K}\Sigma\left\{\frac{f_i^{m-1}}{(f_i-f_1)\ldots(f_i-f_j)\ldots(f_i-\nabla_1)\ldots(f_i-f_m)} + \frac{f_j^{m-1}}{(f_j-f_1)\ldots(f_j-\nabla_1)\ldots(f_j-f_i)\ldots(f_j-f_m)}\right\}0$$

$$= -\frac{1}{K}\Sigma\left\{\frac{f_i^{m-1}}{(f_i-f_1)\ldots(f_i-\nabla_1)\ldots(f_i-f_m)} - \frac{f_j^{m-1}}{(f_j-f_1)\ldots(f_j-\nabla_1)\ldots(f_j-f_m)}\right\}\frac{0}{f_i-f_j}.$$

And if $\alpha_{ij}, \beta_{ij}, \ldots$ be the roots of

$$f_i - f_j = 0$$

when solved with respect to ∇, we shall have

$$\frac{0}{f_i-f_j} = A_{ij}u_{\alpha_{ij}} + B_{ij}u_{\beta_{ij}} + \ldots$$

and

$$u = -\frac{1}{K}\Sigma\left\{\left[\frac{f_i(\alpha_{ij})^{m-1}}{\big(f_i(\alpha_{ij})-f_1(\alpha_{ij})\big)\ldots\big(f_i(\alpha_{ij})-\nabla_1\big)\ldots\big(f_i(\alpha_{ij})-f_m(\alpha_{ij})\big)}\right.\right.$$

$$\left.\left. - \frac{f_j(\alpha_{ij})^{m-1}}{\big(f_j(\alpha_{ij})-f_1(\alpha_{ij})\big)\ldots\big(f_j(\alpha_{ij})-\nabla_1\big)\ldots\big(f_j(\alpha_{ij})-f_m(\alpha_{ij})\big)}\right]A_{ij}u_{\alpha_{ij}}\right.$$

$$\left. + \text{ similar terms in } B_{ij}, \beta_{ij}; \ldots\right\}.$$

And if we assume

$$u_\alpha = (a_0\, a_1 \ldots \chi(x\, y)^\alpha$$
$$u_\beta = (b_0\, b_1 \ldots \chi(x\, y)^\beta$$
$$\ldots\ldots\ldots$$

the values of the coefficients, as affected by the operative factor, may be calculated by formulæ given above.

§ 2.

Let s, s_1, .. be any linear functions of the variables x, y, such as

$$s_i = \alpha_i x + \beta_i y,$$

and let

$$s_i \frac{d}{dx} = u_i, \qquad s_i \frac{d}{dy} = v_i.$$

It is proposed in the first place to investigate expressions for symbols of the form

$$s_1\, s_2 \ldots s_i \frac{d^i}{dx^{i-j}\, dy^j}$$

in terms of the us and vs.

First, as is easily seen,

$$s s_1 \frac{d^2}{dx^2} = s \frac{d}{dx}\left(s_1 \frac{d}{dx} - \alpha_1\right) = u(u_1 - \alpha_1),$$

$$s s_1 \frac{d^2}{dx\, dy} = s \frac{d}{dx} \cdot s_1 \frac{d}{dy} - s u_1 \frac{d}{dy} = s \frac{d}{dy} \cdot s_1 \frac{d}{dx} - s \beta_1 \frac{d}{dx};$$

therefore

$$2 s s_1 \frac{d^2}{dx\, dy} = s \frac{d}{dx}\left(s_1 \frac{d}{dy} - \beta_1\right) + s \frac{d}{dy}\left(s_1 \frac{d}{dx} - \alpha_1\right)$$
$$= u(v_1 - \beta_1) + v(u_1 - \alpha_1).$$

Hence the quadratic system,

$$s_{00} s_{01} \frac{d^2}{dx^2} = u_{00}(u_{01} - \alpha_{01}),$$

$$2 s_{10} s_{11} \frac{d^2}{dx\, dy} = u_{10}(v_{11} - \beta_{11}) + v_{10}(u_{11} - \alpha_{11}),$$

$$s_{20} s_{21} \frac{d^2}{dy^2} = v_{20}(v_{21} - \beta_{21}),$$

or

$$(a_0 x^2 + 2 b_0 xy + c_0 y^2) \frac{d^2}{dx^2} + 2(a_1 x^2 + 2 b_1 xy + c_1 y^2) \frac{d^2}{dx\, dy} + (a_2 x^2 + 2 b_2 xy + c_2 y^2) \frac{d^2}{dy^2}$$
$$= u_{00} u_{01} + u_{10} v_{11} + v_{10} u_{11} + v_{20} v_{21} - \alpha_{01} u_{00} - \beta_{11} u_{10} - \alpha_{11} v_{10} - \beta_{21} v_{20}.$$

Again, developing the following expression by Euler's theorem, and remembering that, since the ss are linear, their second and higher differential coefficients vanish, we have

$$ss_1\frac{d^2}{dx^2}\cdot s_2\frac{d}{dx}=ss_1s_2\frac{d^3}{dx^3}+2ss_1\alpha_2\frac{d^2}{dx^2},$$

or

$$\begin{aligned}ss_1s_2\frac{d^3}{dx^3}&=ss_1\frac{d^2}{dx^2}\left(s_2\frac{d}{dx}-2c_2\right)\\&=s\frac{d}{dx}\left(s_1\frac{d}{dx}-\alpha_1\right)\left(s_2\frac{d}{dx}-2\alpha_2\right)\\&=u(u_1-\alpha_1)(u_2-2\alpha_2).\end{aligned}$$

Again, taking the first two equations of the quadratic system above written, and operating on $s_2\frac{d}{dy}$, $s_2\frac{d}{dx}$ respectively, we have

$$ss_1\frac{d^2}{dx^2}\cdot s_2\frac{d}{dy}=ss_1s_2\frac{d^3}{dx^2\,dy}+2ss_1\alpha_2\frac{d^2}{dx\,dy},$$

$$2ss_1\frac{d^2}{dx\,dy}\cdot s_2\frac{d}{dx}=2ss_1s_2\frac{d^3}{dx^2\,dy}+2ss_1\alpha_2\frac{d^2}{dx\,dy}+2ss_1\beta_2\frac{d^2}{dx^2}.$$

Hence

$$\begin{aligned}3ss_1s_2\frac{d^3}{dx^2\,dy}&=ss_1\frac{d^2}{dx^2}\left(s_2\frac{d}{dy}-2\beta_2\right)+2ss_1\frac{d^2}{dx\,dy}(s_2-2\alpha_2)\\&=u(u_1-\alpha_1)(v_2-2\beta_2)+\{u(v_1-\beta_1)+v(u_1-\alpha_1)\}(u_2-2\alpha_2)\\&=u(u_1-\alpha_1)(v_2-2\beta_2)+u(v_1-\beta_1)(u_2-2\alpha_2)+v(u_1-\alpha_1)(u_2-2\alpha_2).\end{aligned}$$

Hence the cubic system,

$$ss_1s_2\frac{d^3}{dx^3}=u(u_1-\alpha_1)(u_2-2\alpha_2),$$

$$\begin{aligned}3ss_1s_2\frac{d^3}{dx^2\,dy}&=u(u_1-\alpha_1)(v_2-2\beta_2)\\&\quad+u(v_1-\beta_1)(u_2-2\alpha_2)\\&\quad+v(u_1-\alpha_1)(u_2-2\alpha_2),\end{aligned}$$

$$\begin{aligned}3ss_1s_2\frac{d^3}{dx\,dy^2}&=v(v_1-\beta_1)(u_2-2\alpha_2)\\&\quad+v(u_1-\alpha_1)(v_2-2\beta_2)\\&\quad+u(v_1-\beta_1)(v_2-2\beta_2),\end{aligned}$$

$$ss_1s_2\frac{d^3}{dy^3}=v(v_1-\beta_1)(v_2-2\beta_2),$$

in which the ss, us, vs, αs, βs may be furnished with double suffixes, as was done in the quadratic system; and then the sum of the four equations would give the value of

$$(abcd\chi xy)^3\frac{d^3}{dx^3}+(a_1b_1c_1d_1\chi xy)^3\frac{d^3}{dx^2\,dy}+\ldots$$

For the general case, let

$$N_p ss_1\ldots s_{i-1}\frac{d^i}{dx^{i-p}\,dy^p}=A,$$

$$N_{p+1}ss_1\ldots s_{i-1}\frac{d^i}{dx^{i-p-1}\,dy^{p+1}}=B,$$

where

$$N_p=\frac{i(i-1)\,..\,(i-p+1)}{1\,.\,2\,..\,p},\quad N_{p+1}=\frac{i(i-1)\,..\,(i-p)}{1\,.\,2\,..\,(p+1)};$$

so that A and B are two consecutive terms in the system of the degree i. Then operating upon $s_i\frac{d}{dy}$ with A, and upon $s_i\frac{d}{dx}$ with B, in the same way as was done in the case of the third degree, we have

$$\begin{aligned}
As_i\frac{d}{dy}&=N_p s s_1\,..\,s_i\frac{d^{i+1}}{dx^{i-p}dy^{p+1}}\\
&\quad+N_p s s_1\,..\,s_{i-1}(i-p)\alpha_i\frac{d^i}{dx^{i-p-1}dy^{p+1}}\\
&\quad+N_p s s_1\,..\,s_{i-1}p\beta_i\frac{d^i}{dx^{i-p}dy^p},\\
Bs_i\frac{d}{dx}&=N_{p+1}s s_1\,..\,s_i\frac{d^{i+1}}{dx^{i-p}dy^{p+1}}\\
&\quad+N_{p+1}s s_1\,..\,s_{i-1}(i-p-1)\alpha_i\frac{d^i}{dx^{i-p-1}dy^{p+1}}\\
&\quad+N_{p+1}s s_1\,..\,s_{i-1}(p+1)\beta_i\frac{d^i}{dx^{i-p}dy^p}.
\end{aligned}$$

But

$$(p+1)N_{p+1}=(i-p)N_p$$

and

$$\begin{aligned}
N_p+N_{p+1}&=\frac{i(i-1)\,..\,(i-p+1)}{1\,.\,2\,..\,(p+1)}(p+1+i-p)\\
&=\frac{(i+1)i\,..\,(i-p+1)}{1\,.\,2\,..\,(p+1)};
\end{aligned}$$

in other words, N_p+N_{p+1} is equal to the $(p+1)$th coefficient in the case of the degree $(i+1)$. Hence, adding the above written expressions for $As_i\frac{d}{dy}$, $Bs_i\frac{d}{dx}$, and calling the value of N_p+N_{p+1} $_{i+1}N_{p+1}$, we have

$$\begin{aligned}
&{}_{i+1}N_{p+1}s s_1\,..\,s_i\frac{d^{i+1}}{dx^{i-p}dy^{p+1}}\\
&=A\Big(s_i\frac{d}{dy}-i\beta_i\Big)+B\Big(s_i\frac{d}{dx}-i\alpha_i\Big).
\end{aligned}$$

But if it is true (and it has been proved in the cases of 2, 3, . .) that

$$\begin{aligned}
A&=Su(u_1-\alpha_1)\,..\,\big(u_{i-p}-(i-p)\alpha_{i-p}\big)\big(v_{i-p+1}-(i-p+1)\beta_{i-p+1}\big)\,..\,\big(v_{i-1}-(i-1)\beta_{i-1}\big),\\
B&=Su(u_1-\alpha_1)\,..\,\big(u_{i-p-1}-(i-p-1)\alpha_{i-p-1}\big)\big(v_{i-p}-(i-p)\beta_{i-p}\big)\,..\,\big(v_{i-1}-(i-1)\beta_{i-1}\big);
\end{aligned}$$

i. e. if A and B are respectively equal to the sums of all the products of the above forms that can be formed by interchanging the us and vs, so that the total number of the us and of the vs remains constant in each product (viz. $(i-p+1)$ u-factors and $(p-1)$ v-factors in A, and $(i-p)$ u-factors and p v-factors in B); then will $A(v_i-i\beta_i)+B(u_i-i\alpha_i)$

be equal to the sum of all the products of the above form which can be formed with $(i-p)$ u-factors and $(p+1)$ v-factors.

In order to calculate the effect of the operation $Su(u_1-\alpha_1)\ldots$ upon a given function, let

$$V=\Sigma a_i x^{n-i}y^i,$$

then

$$\begin{aligned} uV&=\Sigma(\alpha x+\beta y)(n-i)a_i x^{n-i-1}y^i \\ &=\Sigma\left\{(n-i)\alpha a_i x^{n-i}y^i+(n-i)\beta a_i x^{n-i-1}y^{i+1}\right\} \\ &=\Sigma\left\{(n-i)\alpha a_i+(n-i+1)\beta a_{i-1}\right\}x^{n-i}y^i \\ &=\Sigma\left\{(\alpha+\beta\varepsilon^{-\frac{d}{dx}})(n-i)a_i\right\}x^{n-i}y^i, \end{aligned}$$

in which $\alpha+\beta\varepsilon^{-\frac{d}{dx}}$ must be considered as an operative factor affecting the quantities within the brackets { } alone.

Similarly,

$$(u_1-\alpha_1)V=\Sigma\left\{(n-i-1)\alpha_1 a_i+(n-i+1)\beta_1 a_{i-1}\right\}x^{n-i}y^i;$$

therefore

$$\begin{aligned} u(u_1-\alpha_1)V&=\Sigma\left\{(\alpha+\beta^{-\frac{d}{dx}})(n-i)(n-i-1)\alpha_1 a_i+(\alpha+\beta\varepsilon^{-\frac{d}{dx}})(n-i)(n-i+1)\beta_1 a_{i-1}\right\}x^{n-i}y^i \\ &=\Sigma\left\{(\alpha+\beta\varepsilon^{-\frac{d}{dx}})(\alpha_1+\beta_1\varepsilon^{-\frac{d}{dx}})(n-i)(n-i-1)a_i\right\}x^{n-i}y^i. \end{aligned}$$

And if, as has been proved in the cases 1, 2, .. ,

$$u(u_1-\alpha_1)\ldots(u_m-m\alpha_m)V$$

$$=\Sigma\left\{(\alpha+\beta\varepsilon^{-\frac{\partial}{\partial x}})(\alpha_1+\beta_1\varepsilon^{-\frac{\partial}{\partial x}})\ldots(\alpha_m+\beta_m\varepsilon^{-\frac{\partial}{\partial x}}(n-i)(n-i-1)\ldots(n-i-m)a_i\right\}x^{n-i}y^i,$$

then

$$\left(u_{m+1}-(m+1)\alpha_{m+1}\right)V=\Sigma\left\{(n-i-m-1)\alpha_{m+1}a_i+(n-i+1)\beta_{m+1}a_{i-1}\right\}x^{n-i}y^i;$$

and generally,

$$u(u_1-\alpha_1)\ldots\left(u_{m+1}-(m+1)\alpha_{m+}\right)V$$

$$\begin{aligned} &=\Sigma\left\{(\alpha+\beta\varepsilon^{-\frac{\partial}{\partial x}})(\alpha_1+\beta_1\varepsilon^{-\frac{\partial}{\partial x}})\ldots(\alpha_m+\beta_m\varepsilon^{-\frac{\partial}{\partial x}})(n-i)(n-i-1)\ldots(n-i-m-1)\alpha_{m+1}a_i\right. \\ &\quad\left.+(\alpha+\beta\varepsilon^{-\frac{\partial}{\partial x}})(\alpha_1+\beta_1\varepsilon^{-\frac{\partial}{\partial x}})\ldots(\alpha_m+\beta_m\varepsilon^{-\frac{\partial}{\partial x}})(n-i+1)(n-i)\ldots(n-i-m)\beta_{m+1}a_{i-1}\right\}x^{n-i}y^i \\ &=\Sigma\left\{(\alpha+\beta\varepsilon^{-\frac{\partial}{\partial x}})(\alpha_1+\beta_1\varepsilon^{-\frac{\partial}{\partial x}})\ldots(\alpha_{m+1}+\beta_{m+1}\varepsilon^{-\frac{\partial}{\partial x}})(n-i)(n-i-1)\ldots(n-i-m-1)a_i\right\}x^{n-i}y^i. \end{aligned}$$

Again,

$$\begin{aligned} vV&=\Sigma\left\{(\alpha x+\beta y)ia_i\right\}x^{n-i}y^i \\ &=\Sigma\left\{\alpha(i+1)a_{i+1}+\beta ia_i\right\}x^{n-i}y^i \\ &=\Sigma\left\{(\alpha\varepsilon^{\frac{\partial}{\partial y}}+\beta)ia_i\right\}x^{n-i}y^i \\ (v_1-\beta_1)V&=\Sigma\left\{\alpha_1(i+1)a_{i+1}+\beta_1(i-1)a_i\right\}x^{n-i}y^i \\ v(v_1-\beta_1)V&=\Sigma\left\{(\alpha\varepsilon^{\frac{\partial}{\partial y}}+\beta)i[\alpha_1(i+1)a_{i+1}+\beta_1(i-1)a_i]\right\}x^{n-i}y^i \\ &=\Sigma\left\{(\alpha\varepsilon^{\frac{\partial}{\partial y}}+\beta)(\alpha_1\varepsilon^{\frac{\partial}{\partial y}}+\beta_1)i(i-1)a_i\right\}x^{n-i}y^i. \end{aligned}$$

And in the same way as in the case of the us, it may be shown that

$$v(v_1-\beta_1)..(v_m-m\beta_m)\mathrm{V}$$
$$=\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)(\alpha_1 s^{\frac{\partial}{\partial i}}+\beta_1)..(\alpha_m+\beta_m s^{\frac{\partial}{\partial i}})i(i-1)..(i-m)a_i\right\}x^{n-i}y^i.$$

Again, for the intermediate terms of the system,

$$u(v_1-\beta_1)\mathrm{V}=\Sigma\left\{(\alpha+\beta s^{\frac{\partial}{\partial i}})(n-i)[(i+1)\alpha_1 a_{i+1}+(i-1)\beta_1\alpha_i]\right\}x^{n-i}y^i$$
$$=\Sigma\left\{(\alpha^{\frac{\partial}{\partial i}}+\beta)(n-i+1)[i\alpha_1\alpha_i+(i-2)\beta_1 a_{i-1}]\right\}x^{n-i}y^i$$
$$v(u_1-\alpha_1)\quad=\Sigma\left\{(\alpha^{\frac{\partial}{\partial i}}+\beta)i[(n-i-1)\alpha_1 a_i+(n-i+1)\beta_1 a_{i-1}]\right\}x^{n-i}y^i.$$

Hence

$$\left\{u(v_1-\beta_1)+v(u_1-\alpha_1)\right\}\mathrm{V}$$
$$=2\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)[(n-i)i\alpha_1 a_i+(n-i+1)(i-1)\beta_1 a_{i-1}]\right\}x^{n-i}y^i$$
$$=2\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)(\alpha_1+\beta_1 s^{-\frac{\partial}{\partial i}})(n-i)ia_i\right\}x^{n-i}y^i.$$

Again,

$$\left\{u(v_1-\beta_1)+v(u_1-\alpha_1)\right\}(u_2-2\alpha_2)\mathrm{V}$$
$$=2\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)(\alpha_1+\beta_1 s^{-\frac{\partial}{\partial i}})(n-i)i[(n-i-2)\alpha_2 a_i+(n-i+1)\beta_2 a_{i-1}]\right\}x^{n-i}y^i,$$
$$u(u_1-\alpha_1)(v_2-2\beta_2)\mathrm{V}$$
$$=\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)(\alpha_1+\beta_1 s^{-\frac{\partial}{\partial i}})(n-i+1)(n-i)[\alpha_2 ia_i+\beta_2(i-3)a_{i-1}]\right\}x^{n-i}y^i.$$

Hence

$$u(u_1-\alpha_1)(v_2-2\beta_2)+u(v_1-\beta_1)(u_2-2\alpha_2)+v(u_1-\alpha_1)(u_2-2\alpha_2)$$
$$=3\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)(\alpha_1+\beta_1 s^{-\frac{\partial}{\partial i}})[(n-i)i\alpha_2 a_2(n-i-1)+(n-i+1)(n-i)\beta_2 a_{i-1}(i-1)]\right\}x^{n-i}y^i$$
$$=3\Sigma\left\{(\alpha s^{\frac{\partial}{\partial i}}+\beta)(\alpha_1+\beta_1 s^{-\frac{\partial}{\partial i}})(\alpha_2+\beta_2 s^{-\frac{\partial}{\partial i}})(n-i)(n-i-1)ia_i\right\}x^{n-i}y^i.$$

Again, for the general term, let

$$\mathrm{A}={}_m\mathrm{N}_{p-1}s s_1..s_{m-1}\frac{d^m}{dx^{m-p+1}dy^{p-1}}$$
$$={}_m\mathrm{N}_{p-1}(\alpha+\beta s^{-\frac{\partial}{\partial i}})..(\alpha_{m-p}+\beta_{m-p}s^{-\frac{\partial}{\partial i}})(\alpha_{m-p+1}s^{\frac{\partial}{\partial i}}+\beta_{m-p+1})..(\alpha_{m-1}s^{\frac{\partial}{\partial i}}+\beta_{m-1})(n-i)..(n-i-m+p)i..(i-p+2),$$

$$\mathrm{B}={}_m\mathrm{N}_{p-1}s s_1..s_{m-1}\frac{d^m}{dx^{m-p}dy^p}$$
$$={}_m\mathrm{N}_{p-1}(\alpha+\beta s^{-\frac{\partial}{\partial i}})..(\alpha_{m-p-1}+\beta_{m-p-1}s^{-\frac{\partial}{\partial i}})(\alpha_{m-p}s^{\frac{\partial}{\partial i}}+\beta_{m-p})..(\alpha_{m-1}s^{\frac{\partial}{\partial i}}+\beta_{m-1})(n-i)..(n-i-m+p-1)i..(i-p+1).$$

Also let

$$\mathrm{K}=(\alpha+\beta s^{-\frac{\partial}{\partial i}})..(\alpha_{m-p}+\beta_{m-p}s^{-\frac{\partial}{\partial i}})(\alpha_{m-p+1}s^{\frac{\partial}{\partial i}}+\beta_{m-p+1})..(\alpha_{m-1}s^{\frac{\partial}{\partial i}}+\beta_{m-1}).$$

Then changing $\alpha_{m-p}\varepsilon^{\frac{\partial}{\partial i}}+\beta_{m-p}$, in B, into $\alpha_{m-p}+\beta_{m-p}\varepsilon^{\frac{\partial}{\partial i}}$, and compensating the change by writing $(i+1)$ for i in the numerical factors to the right, we have

$$A=K\,{}_mN_{p-1}(n-i)\,..\,(n-i-m+p)i\,..\,(i-p+2),$$
$$B=K\,{}_mN_p(n-i-1)\,..\,(n-i-m+p)(i+1)\,..\,(i-p+2)\varepsilon^{\frac{\partial}{\partial i}},$$

the factor $\varepsilon^{\frac{\partial}{\partial i}}$ having been added in order to indicate that i must be changed into $(i+1)$ in the expression upon which B will presently be made to operate. Then making

$$H=(n-i-1)\,..\,(n-i-m+p)i\,..\,(i-p+2),$$
$$C=\{A(v_m-m\beta_m)+B(u_m-m\alpha_m)\}V$$
$$=\Sigma\Big[KH\,{}_mN_{p-1}(n-i)\{(i+1)\alpha_m a_{i+1}+(i-m)\beta_m a_i\}$$
$$+KH\,{}_mN_p\ (i+1)\{(n-i-m-1)\alpha_m a_{i+1}+(n-i)\beta_m a_i\}\Big]x^{n-i}y^i$$
$$=\Sigma\Big[KH\{(i+1)[(n-i)\,{}_mN_{p-1}+(n-i-m-1)\,{}_mN_p]\alpha_m a_{i+1}$$
$$+(n-i)[(i-m)\,{}_mN_{p-1}+(i+1)\ \ {}_mN_p]\beta_m a_i\}\Big].$$

Now

$$(n-i)\,{}_mN_{p-1}+(n-i-m-1)\,{}_mN_p$$
$$=(n-i)({}_mN_{p-1}+{}_mN_p)-(m+1)\,{}_mN_p$$
$$=(n-i)\,{}_{m+1}N_p-(m-p+1)\,{}_{m+1}N_p$$
$$=(n-i-m+p-1)\,{}_{m+1}N_p,$$

and

$$(i-m)\,{}_mN_{p-1}+(i+1)\,{}_mN_p$$
$$=(i+1)({}_mN_{p-1}+{}_mN_p)-(m+1)\,{}_mN_{p-1}$$
$$=(i+1)\,{}_{m+1}N_p-p\,{}_{m+1}N_p$$
$$=(i+1-p)\,{}_{m+1}N_p.$$

Hence

$$C=\Sigma\Big[{}_{m+1}N_pKH\{(n-i-m+p-1)(i+1)\alpha_m a_{i+1}+(n-i)(i-p+1)\beta_m a_i\}\Big]x^{n-i}y^i$$
$$=\Sigma\Big[{}_{m+1}N_pK(\alpha_m\varepsilon^{\frac{\partial}{\partial i}}+\beta_m)(n-i)\,..\,(n-i-m+p)i\,..\,(i-p+1)a_i\Big]x^{n-i}y^i$$
$$=\Sigma\Big[{}_{m+1}N_p(\alpha+\beta\varepsilon^{-\frac{\partial}{\partial i}})\,..\,(\alpha_{m-p}+\beta_{m-p}\varepsilon^{-\frac{\partial}{\partial i}})(\alpha_{m-p+1}\varepsilon^{\frac{\partial}{\partial i}}+\beta_{m-p+1})\,..\,(\alpha_m\varepsilon^{\frac{\partial}{\partial i}}+\beta_m)$$
$$(n-i)\,..\,(n-i-m+p)i\,..\,(i-p+1)a_i\Big]x^{n-i}y^i,$$

which proves the formula generally.

This expression may, however, be transformed into a more convenient shape, as follows. Let

$$s_1 s_2\,..\,s_m=(a\,a_1\,..\,a_m)(xy)^m,$$

then

$$(\alpha_1+\beta_1\varepsilon^{-\frac{\partial}{\partial i}})(\alpha_2+\beta_2\varepsilon^{-\frac{\partial}{\partial i}})\,..\,(\alpha_m+\beta_m\varepsilon^{-\frac{\partial}{\partial i}})=(a\,a_1\,..\,a_m)(1\,\varepsilon^{-\frac{\partial}{\partial i}})^m.$$

And if

$$\mathrm{U}=(\mathrm{a}\,\mathrm{a}_1\,..\,\mathrm{a}_m)(x\,y)^m,$$
$$\Upsilon=(\mathrm{a}\,\mathrm{a}_1\,..\,\mathrm{a}_m)(\varepsilon^{\frac{d}{di}}1)^m,$$
$$\mathrm{F}=(a\,a_1\,..\,a_m)(x\,y)^n,$$
$$\mathrm{P}_i={}_n\mathrm{N}_i i(i-1)\,..\,(i-m+1),$$

then, since

$$\begin{aligned}&(n-i+m)(n-i+m-1)\,..\,(n-i+p+1)(i-m)\,..\,(i-m-p+1)\varepsilon^{-m\frac{d}{di}}{}_n\mathrm{N}_i\\ &=(n-i+m)(n-i+m-1)\,..\,(n-i+p+1)(i-m)\,..\,(i-m-p+1){}_n\mathrm{N}_{i-m}\varepsilon^{-\frac{d}{di}}\\ &={}_n\mathrm{N}_{i-p}(i-m+1)(i-m+2)\,..\,(i-p)(i-m)(i-m-1)\,..\,(i-m-p+1)\varepsilon^{-\frac{d}{di}}\\ &={}_n\mathrm{N}_{i-p}(i-p)(i-p-1)\,..\,(i-m-p+1)\varepsilon^{-m\frac{d}{di}},\end{aligned}$$

we have

$$\begin{aligned}\mathrm{U}\frac{d^m\mathrm{F}}{dx^{m-p}dy^p}&=\Sigma\Big\{\Upsilon\varepsilon^{-(m-p)\frac{d}{di}}(n-i)\,..\,(n-i-m+p+1)i\,..\,(i-p+1){}_n\mathrm{N}_i a_i\Big\}x^{n-i}y^i\\ &=\Sigma\Big\{\Upsilon\varepsilon^{p\frac{d}{di}}(n-i+m)\,..\,(n-i+p+1)(i-m)\,..\,(i-m-p+1)\varepsilon^{-m\frac{d}{di}}{}_n\mathrm{N}_i a_i\Big\}x^{n-i}y^i\\ &=\Sigma\Big\{\Upsilon\varepsilon^{p\frac{d}{di}}\mathrm{P}_{i-p}\varepsilon^{-m\frac{d}{di}}a_i\Big\}x^{n-i}y^i\\ &=\Sigma\Big\{\Upsilon\mathrm{P}_i\varepsilon^{p\frac{d}{di}}a_{i-m}\Big\}x^{n-i}y^i.\end{aligned}$$

Hence

$$\begin{aligned}&\mathrm{U}_0\frac{d^m\mathrm{F}}{dx^m}+\frac{m}{1}\mathrm{U}_1\frac{d^m\mathrm{F}}{dx^{m-1}dy}+\,..\,+\mathrm{U}_m\frac{d^m\mathrm{F}}{dy^m}\\ &=\Sigma\Big\{\Big[\Upsilon_0\mathrm{P}_i+\frac{m}{1}\Upsilon_1\mathrm{P}_i\varepsilon^{\frac{d}{di}}+\,..\,+\Upsilon_m\mathrm{P}_i\varepsilon^{m\frac{d}{di}}\Big]a_{i-m}\Big\}x^{n-i}y^i\\ &=\Sigma\Big\{\Big[\Big(\mathrm{a}_{00}\varepsilon^{m\frac{d}{di}}+\frac{m}{1}\mathrm{a}_{01}\varepsilon^{(m-1)\frac{d}{di}}+\,..\,+\mathrm{a}_{0m}\Big)\mathrm{P}_i\\ &\quad+\frac{m}{1}\Big(\mathrm{a}_{10}\varepsilon^{m\frac{d}{di}}+\frac{m}{1}\mathrm{a}_{11}\varepsilon^{(m-1)\frac{d}{di}}+\,..\,+\mathrm{a}_{1m}\Big)\mathrm{P}_i\varepsilon^{\frac{d}{di}}\\ &\quad+\,\ldots\\ &\quad+\,\Big(\mathrm{a}_{m0}\varepsilon^{m\frac{d}{di}}+\frac{m}{1}\mathrm{a}_{m1}\varepsilon^{(m-1)\frac{d}{di}}+\,..\,+\mathrm{a}_{mm}\Big)\mathrm{P}_i\varepsilon^{m\frac{d}{di}}\Big]a_{i-m}\Big\}x^{n-i}y^i;\end{aligned}$$

and writing

$$\frac{m(m-1)\,..\,(m-q+1)}{1:2\,..\,q}=\mathrm{M}_q,$$

the above expression

$$\begin{aligned}&=\Sigma\Big\{\big[\mathrm{M}_0\mathrm{a}_{0,m}\mathrm{P}_i\\ &\quad+(\mathrm{M}_1\mathrm{a}_{0,m-1}\mathrm{P}_{i+1}+\mathrm{M}_1\mathrm{a}_{1,m}\mathrm{P}_i)\varepsilon^{\frac{d}{di}}\\ &\quad+(\mathrm{M}_0\mathrm{M}_2\mathrm{a}_{0,m-2}\mathrm{P}_{i+2}+\mathrm{M}_1^2\mathrm{a}_{1,m-1}\mathrm{P}_{i+1}+\mathrm{M}_2\mathrm{M}_0\mathrm{a}_{2,m}\mathrm{P}_i)\varepsilon^{2\frac{d}{di}}\\ &\quad+\,\ldots\\ &\quad+(\mathrm{M}_1\mathrm{a}_{m-1,0}\mathrm{P}_{i+m}+\mathrm{M}_1\mathrm{a}_{m,1}\mathrm{P}_{i+m-1})\varepsilon^{(2m-1)\frac{d}{di}}\\ &\quad+\,\mathrm{M}_0\mathrm{a}_{m,0}\mathrm{P}_{i+m}\varepsilon^{2m\frac{d}{di}}\big]a_{i-m}\Big\}x^{n-i}y^i;\end{aligned}$$

in which all terms will vanish for which

$$i-m<0, \text{ and } i+m>n.$$

In order to determine the effect of the operation

$$\left[\left(U_0U_1..\right)\left(\frac{d}{dx}\frac{d}{dy}\right)^m\right]^{-1}$$

on a given function, we may proceed, as before, by making

$$\left[\left(U_0U_1..\right)\left(\frac{d}{dx}\frac{d}{dy}\right)^m\right]^{-1}(A_0A_1..)(xy)^n=(a_0a_1..)(xy)^n,$$

or

$$(A_0A_1..)(xy)^n=\left(U_0U_1..\right)\left(\frac{d}{dx}\frac{d}{dy}\right)^m(a_0a_1..)(xy)^n;$$

and then the coefficients $a_0a_1..$ will be given by the system, of which the following is a type:

$$\begin{aligned}A_i=&[M_0a_{0,m}P_i\\&+(M_1a_{0,m-1}P_{i+1}+M_1a_{1m}P_i)\phi^{\frac{d}{dx}}\\&+\ldots]a_{i-m},\end{aligned}$$

as above. In order to solve these equations for $a\,a_1..$, we may regard the expression within the brackets [ ] as a function of $\phi^{\frac{d}{dx}}$; and resolving it into its factors, we may proceed by way of operations instead of direct elimination. Let $p_1, p_2, .. p_{2m}$ be the roots; then

$$A_i=a_{m,0}P_{i+m}(\phi^{\frac{d}{dx}}-p_1)(\phi^{\frac{d}{dx}}-p_2)..(\phi^{\frac{d}{dx}}-p_{2m})a_{i-m}$$

and

$$a_{i-m}=\quad(\phi^{\frac{d}{dx}}-p_1)^{-1}(\phi^{\frac{d}{dx}}-p_2)^{-1}..(\phi^{\frac{d}{dx}}-p_{2m})^{-1}\frac{A_i}{a_{m,0}P_{i+m}}.$$

But

$$\begin{aligned}(\phi^{\frac{d}{dx}}-p_1)^{-1}\frac{A_i}{P_{i+m}}&=-\frac{1}{p_1}\left(1+\frac{\phi^{\frac{d}{dx}}}{p_1}+\frac{\phi^{2\frac{d}{dx}}}{p_1^2}+..\right)\frac{A_i}{P_{i+m}}\\&=-\frac{1}{p_1}\left(\frac{A_i}{P_{i+m}}+\frac{1}{p_1}\frac{A_{i+1}}{P_{i+m+1}}+..+\frac{A_n}{p_1^{n-i}P_{n+m+1}}\right)\\(\phi^{\frac{d}{dx}}-p_1)^{-1}(\phi^{\frac{d}{dx}}-p_2)^{-1}&\frac{A_i}{P_{i+m}}\\&=(-)^2\frac{1}{p_1p_2}\left\{\left(\frac{A_i}{P_{i+m}}+\frac{1}{p_1}\frac{A_{i+1}}{P_{i+m+1}}+..\frac{1}{p_1^{n-i}}\frac{A_n}{P_{n+m+1}}\right)\right.\\&\quad+\frac{1}{p_2}\left(\frac{A_{i+1}}{P_{i+m+1}}+\frac{1}{p_1}\frac{A_{i+2}}{P_{i+m+2}}+..\frac{1}{p_1^{n-i-1}}\frac{A_n}{P_{n+m+1}}\right)\\&\quad\left.+\quad.\quad.\quad.\quad.\quad.\quad.\right\}\\&=(-)^2\frac{1}{p_1p_2}\left\{\frac{A_i}{P_{i+m}}+\left(\frac{1}{p_1},\frac{1}{p_2}\right)\frac{A_{i+1}}{P_{i+m+1}}+..\left(\frac{1}{p_1},\frac{1}{p_2}\right)^{n-i}\frac{A_n}{P_{n+m+1}}\right\};\end{aligned}$$

and consequently

$$a_{i-m}=(-)^{2m}\frac{1}{a_{m,0}p_1p_2..p_{2m}}\left\{\frac{A_i}{P_{i+m}}+\left(\frac{1}{p_1},\frac{1}{p_2}..\frac{1}{p_{2m}}\right)\frac{A_{i+1}}{P_{i+m+1}}+..\left(\frac{1}{p_1}\frac{1}{p_2}..\frac{1}{p_{2m}}\right)^{n-i}\frac{A_n}{P_{n+m+1}}\right\}.$$

The expression $(s^{\frac{d}{dx}}-p_1)^{-1}(s^{\frac{d}{dx}}-p_2)^{-1}..(s^{\frac{d}{dx}}-p_{2m})^{-1}$ may be resolved into its partial fractions in the usual way by writing

$$C_1=\frac{p_1^{2m-1}}{(p_1-p_2)(p_1-p_3)..(p_1-p_{2m})},\quad C_2=\frac{p_2^{2m-1}}{(p_2-p_1)(p_2-p_3)..(p_2-p_{2m})},\ ..$$

and then it takes the form

$$\frac{C_1}{s^{\frac{d}{dx}}-p_1}+\frac{C_2}{s^{\frac{d}{dx}}-p_2}+..\frac{C_{2m}}{s^{\frac{d}{dx}}-p_{2m}}$$

$$=\frac{C_1}{p_1}+\frac{C_2}{p_2}+..+\left(\frac{C_1}{p_1^2}+\frac{C_2}{p_2^2}+..\right)s^{\frac{d}{dx}}+..,$$

giving

$$a_{i-m}=\frac{1}{a_{m,0}}\left\{\left(\frac{C_1}{p_1}+\frac{C_2}{p_2}+..\right)\frac{A_i}{P_{i+m}}+\left(\frac{C_1}{p_1^2}+\frac{C_2}{p_2^2}+..\right)\frac{A_{i+1}}{P_{i+m+1}}+..\left(\frac{C_1}{p_1^{n-i+1}}+\frac{C_2}{p_2^{n-i+1}}+..\right)\frac{A_n}{P_{n+m+1}}\right\}.$$

§ 3. *The case of* s_i *being any function of* x, y.

Although it seems doubtful, on account of their complexity, whether the following formulæ are likely to be of much practical use, it is still worth while to complete the theory by considering the most general case where s_i, instead of being linear, is any function whatever of x, y.

Since

$$s_1s\frac{d^2}{dx^2}=s_1\frac{d}{dx}.s\frac{d}{dx}-s_1\frac{ds}{dx}\frac{d}{dx}$$

$$=s\frac{d}{dx}.s_1\frac{d}{dx}-s\frac{ds_1}{dx}\frac{d}{dx},$$

therefore

$$2s_1s\frac{d^2}{dx^2}=\left(s_1\frac{d}{dx}-\frac{ds}{dx}\right)s\frac{d}{dx}+\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_1\frac{d}{dx}.$$

Again,

$$s_2s_1s\frac{d^3}{dx^3}=s\frac{d}{dx}.s_2s_1\frac{d^2}{dx^2}-s\frac{ds_2s_1}{dx}\frac{d^2}{dx^2}$$

$$=s_1\frac{d}{dx}.ss_2\frac{d^2}{dx^2}-s_1\frac{dss_2}{dx}\frac{d^2}{dx^2}$$

$$=s_2\frac{d}{dx}.s_1s\frac{d^2}{dx^2}-s_2\frac{ds_1s}{dx}\frac{d^2}{dx^2},$$

Hence

$$6s_2s_1s\frac{d^3}{dx^3}=\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)2s_2s_1\frac{d^2}{dx^2}$$
$$+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)2s\,s_2\frac{d^2}{dx^2}$$
$$+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)2s_1s\frac{d^2}{dx^2}$$
$$=\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s_2\frac{d}{dx}+\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)\left(s_2\frac{d}{dx}-\frac{ds_2}{dx}\right)s_1\frac{d}{dx}$$
$$+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)\left(s_2\frac{d}{dx}-\frac{ds_2}{dx}\right)s\frac{d}{dx}+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_2\frac{d}{dx}$$
$$+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_1\frac{d}{dx}+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s\frac{d}{dx}$$
$$=s\frac{d}{dx}s_1\frac{d}{dx}s_2\frac{d}{dx}-2\frac{ds}{dx}s_1\frac{d}{dx}s_2\frac{d}{dx}-\frac{ds_1}{dx}s\frac{d}{dx}s_2\frac{d}{dx}+2\frac{ds}{dx}\frac{ds_1}{dx}s_2\frac{d}{dx}-s\frac{d^2s_1}{dx^2}s_2\frac{d}{dx}$$
$$+s\frac{d}{dx}s_2\frac{d}{dx}s_1\frac{d}{dx}-2\frac{ds}{dx}s_2\frac{d}{dx}s_1\frac{d}{dx}-\frac{ds_2}{dx}s\frac{d}{dx}s_1\frac{d}{dx}+2\frac{ds}{dx}\frac{ds_2}{dx}s_1\frac{d}{dx}-s\frac{d^2s_2}{dx^2}s_1\frac{d}{dx}$$
$$+s_1\frac{d}{dx}s_2\frac{d}{dx}s\frac{d}{dx}-2\frac{ds_1}{dx}s_2\frac{d}{dx}s\frac{d}{dx}-\frac{ds_2}{dx}s_1\frac{d}{dx}s\frac{d}{dx}+2\frac{ds_1}{dx}\frac{ds_2}{dx}s\frac{d}{dx}-s_1\frac{d^2s_2}{dx^2}s\frac{d}{dx}$$
$$+s_1\frac{d}{dx}s\frac{d}{dx}s_2\frac{d}{dx}-2\frac{ds_1}{dx}s\frac{d}{dx}s_2\frac{d}{dx}-\frac{ds}{dx}s_1\frac{d}{dx}s_2\frac{d}{dx}+2\frac{ds_1}{dx}\frac{ds}{dx}s_2\frac{d}{dx}-s_1\frac{d^2s}{dx^2}s_2\frac{d}{dx}$$
$$+s_2\frac{d}{dx}s\frac{d}{dx}s_1\frac{d}{dx}-2\frac{ds_2}{dx}s\frac{d}{dx}s_1\frac{d}{dx}-\frac{ds}{dx}s_2\frac{d}{dx}s_1\frac{d}{dx}+2\frac{ds_2}{dx}\frac{ds}{dx}s_1\frac{d}{dx}-s_2\frac{d^2s}{dx^2}s_1\frac{d}{dx}$$
$$+s_2\frac{d}{dx}s_1\frac{d}{dx}s\frac{d}{dx}-2\frac{ds_2}{dx}s_1\frac{d}{dx}s\frac{d}{dx}-\frac{ds_2}{dx}s_1\frac{d}{dx}s\frac{d}{dx}+2\frac{ds_2}{dx}\frac{ds_1}{dx}s\frac{d}{dx}-s_2\frac{d^2s_1}{dx^2}s\frac{d}{dx}$$
$$=s\frac{d}{dx}s_1\frac{d}{dx}s_2\frac{d}{dx}+s\frac{d}{dx}s_2\frac{d}{dx}s_1\frac{d}{dx}+s_1\frac{d}{dx}s_2\frac{d}{dx}s\frac{d}{dx}+s_1\frac{d}{dx}s\frac{d}{dx}s_2\frac{d}{dx}+s_2\frac{d}{dx}s\frac{d}{dx}s_1\frac{d}{dx}+s_2\frac{d}{dx}s_1\frac{d}{dx}s\frac{d}{dx}$$
$$-3\frac{ds}{dx}\left(s_1\frac{d}{dx}s_2\frac{d}{dx}+s_2\frac{d}{dx}s_1\frac{d}{dx}\right)-3\frac{ds_1}{dx}\left(s_2\frac{d}{dx}s\frac{d}{dx}+s\frac{d}{dx}s_2\frac{d}{dx}\right)-3\frac{ds_2}{dx}\left(s\frac{d}{dx}s_1\frac{d}{dx}+s_1\frac{d}{dx}s\frac{d}{dx}\right)$$
$$+\left(4\frac{ds_1}{dx}\frac{ds_2}{dx}-s_1\frac{d^2s_2}{dx^2}-s_2\frac{d^2s_1}{dx^2}\right)s\frac{d}{dx}$$
$$+\left(4\frac{ds_2}{dx}\frac{ds}{dx}-s_2\frac{d^2s}{dx^2}-s\frac{d^2s_2}{dx^2}\right)s_1\frac{d}{dx}$$
$$+\left(4\frac{ds}{dx}\frac{ds_1}{dx}-s_1\frac{d^2s_1}{dx^2}-s_1\frac{d^2s}{dx^2}\right)s_2\frac{d}{dx}.$$

Suppose that the above law holds good for m factors; then

$$1.2\,..\,m\,ss_1\,..\,s_m\frac{d^m}{dx^m}=\Sigma\left(s\frac{d}{dx}-(m-1)\frac{ds}{dx}\right)\left(s_1\frac{d}{dx}-(m-2)\frac{ds_1}{dx}\right)..\,s_{m-1}\frac{d}{dx},$$

where Σ indicates that the sum of all products formed by the interchanges of the suffixes $0, 1, .. m-1$, is to be taken. Then

$$1.2..(m+1)ss_1..s_m\frac{d^{m+1}}{dx^{m+1}}$$

$$=s\frac{d}{dx}1.2..ms_1s_2..s_m\frac{d^m}{dx^m}-1.2..ms\frac{ds_1s_2..s_m}{dx}\frac{d^m}{dx^m}$$

$$+s_1\frac{d}{dx}1.2..mss_2..s_m\frac{d^m}{dx^m}-1.2..ms_1\frac{dss_2..s_m}{dx}\frac{d^m}{dx^m}$$

$$+\ldots$$

$$=\left(s\frac{d}{dx}-m\frac{ds}{dx}\right)1.2..ms_1s_2..s_m\frac{d^m}{dx^m}$$

$$+\left(s_1\frac{d}{dx}-m\frac{ds_1}{dx}\right)1.2..mss_2..s_m\frac{d^m}{dx^m}$$

$$+\ldots$$

$$=\Sigma\left(s\frac{d}{dx}-m\frac{ds}{dx}\right)\left(s_1\frac{d}{dx}-(m-1)\frac{ds_1}{dx}\right)..s_m\frac{d}{dx},$$

which proves it in the general case.

Again,

$$ss_1\frac{d^2}{dx\,dy}=s\frac{d}{dx}s_1\frac{d}{dy}-s\frac{ds_1}{dx}\frac{d}{dy}$$

$$=s\frac{d}{dy}s_1\frac{d}{dx}-s\frac{ds_1}{dy}\frac{d}{dx}$$

$$=s_1\frac{d}{dx}s\frac{d}{dy}-s_1\frac{ds}{dx}\frac{d}{dy}$$

$$=s_1\frac{d}{dy}s\frac{d}{dx}-s_1\frac{ds}{dy}\frac{d}{dx}.$$

Hence

$$2ss_1\frac{d^2}{dx\,dy}=\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_1\frac{d}{dy}+\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s\frac{d}{dy}$$

$$=\left(s\frac{d}{dy}-\frac{ds}{dy}\right)s_1\frac{d}{dx}+\left(s_1\frac{d}{dy}-\frac{ds_1}{dy}\right)s\frac{d}{dx}.$$

Again,

$$ss_1s_2\frac{d^3}{dx^2dy}=s\frac{d}{dy}s_1s_2\frac{d^2}{dx^2}-\frac{ds_1}{dy}s_2s\frac{d^2}{dx^2}-\frac{ds_2}{dy}ss_1\frac{d^2}{dx^2}$$

$$=-\frac{ds}{dy}s_1s_2\frac{d^2}{dx^2}+s_1\frac{d}{dy}s_2s\frac{d^2}{dx^2}-\frac{ds_2}{dy}ss_1\frac{d^2}{dx^2}$$

$$=-\frac{ds}{dy}s_1s_2\frac{d^2}{dx^2}-\frac{ds_1}{dy}s_2s\frac{d^2}{dx^2}+s_2\frac{d}{dy}ss_1\frac{d^2}{dx^2}.$$

Hence

$$6ss_1s_2\frac{d^3}{dx^2dy}=\left(s\frac{d}{dy}-2\frac{ds}{dy}\right)2s_1s_2\frac{d^2}{dx^2}$$

$$+\left(s_1\frac{d}{dy}-2\frac{ds_1}{dy}\right)2s_2s\frac{d^2}{dx^2}$$

$$+\left(s_2\frac{d}{dy}-2\frac{ds_2}{dy}\right)2ss_1\frac{d^2}{dx^2}.$$

Again,

$$ss_1s_2\frac{d^3}{dx^2\,dy}=s\frac{d}{dx}s_1s_2\frac{d^2}{dx\,dy}-\frac{ds_1}{dx}s_2s\frac{d^2}{dx\,dy}-\frac{ds_2}{dx}ss\frac{d^2}{dx\,dy}$$

$$=-\frac{ds}{dx}s_1s_2\frac{d^2}{dx\,dy}+s_1\frac{d}{dx}s_2s\frac{d^2}{dx\,dy}-\frac{ds_2}{dx}ss_1\frac{d^2}{dx\,dy}$$

$$=-\frac{ds}{dx}s_1s_2\frac{d^2}{dx\,dy}-\frac{ds_1}{dx}s_2s\frac{d^2}{dx\,dy}+s_2\frac{d}{dx}ss_1\frac{d^2}{dx\,dy},$$

whence

$$6ss_1s_2\frac{d^3}{dx^2\,dy}=\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)2s_1s_2\frac{d^3}{dx\,dy}$$

$$+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)2s_2s\frac{d^2}{dx\,dy}$$

$$+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)2ss_1\frac{d^2}{dx\,dy};$$

and consequently the expression $6ss_1s_2\frac{d^3}{dx^2dy}$ admits of three equivalents, as follows:

$$6ss_1s_2\frac{d^3}{dx^2\,dy}$$

$$=\left(s\frac{d}{dy}-2\frac{ds}{dy}\right)\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s_2\frac{d}{dx}+\left(s\frac{d}{dy}-2\frac{ds}{dy}\right)\left(s_2\frac{d}{dx}-\frac{ds_2}{dx}\right)s\frac{d}{dx}$$

$$+\left(s_1\frac{d}{dy}-2\frac{ds_1}{dy}\right)\left(s_2\frac{d}{dx}-\frac{ds_2}{dx}\right)s\frac{d}{dx}+\left(s_1\frac{d}{dy}-2\frac{ds_1}{dy}\right)\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_2\frac{d}{dx}$$

$$+\left(s_2\frac{d}{dy}-2\frac{ds_2}{dy}\right)\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_1\frac{d}{dx}+\left(s_2\frac{d}{dy}-2\frac{ds_2}{dy}\right)\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s\frac{d}{dx}$$

$$=\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)\left(s_1\frac{d}{dy}-\frac{ds_1}{dy}\right)s_2\frac{d}{dx}+\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)\left(s_2\frac{d}{dy}-\frac{ds_2}{dy}\right)s_1\frac{d}{dx}$$

$$+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)\left(s_2\frac{d}{dy}-\frac{ds_2}{dy}\right)s\frac{d}{dx}+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)\left(s\frac{d}{dy}-\frac{ds}{dy}\right)s_2\frac{d}{dx}$$

$$+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)\left(s\frac{d}{dy}-\frac{ds}{dy}\right)s_1\frac{d}{dx}+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)\left(s_1\frac{d}{dy}-\frac{ds_1}{dy}\right)s\frac{d}{dx}$$

$$=\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s_2\frac{d}{dy}+\left(s\frac{d}{dx}-2\frac{ds}{dx}\right)\left(s_2\frac{d}{dx}-\frac{ds_2}{dx}\right)s_1\frac{d}{dy}$$

$$+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)\left(s_2\frac{d}{dx}-\frac{ds_2}{dx}\right)s\frac{d}{dy}+\left(s_1\frac{d}{dx}-2\frac{ds_1}{dx}\right)\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_2\frac{d}{dy}$$

$$+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)\left(s\frac{d}{dx}-\frac{ds}{dx}\right)s_1\frac{d}{dy}+\left(s_2\frac{d}{dx}-2\frac{ds_2}{dx}\right)\left(s_1\frac{d}{dx}-\frac{ds_1}{dx}\right)s\frac{d}{dy}.$$

In short, in order to change the expression for $6ss_1s_2\frac{d^3}{dx^3}$ into that for $6ss_1s_2\frac{d^3}{dx^2\,dy}$, we

have only to write $\frac{d}{dy}$ for $\frac{d}{dx}$ in *one* of the factors of each term; the *same* factor being changed throughout.

Writing x for y, and y for x, we have the corresponding expression for $6ss_1s_2\frac{d^3}{dxdy^2}$. And a train of reasoning similar to that used in calculating $1.2..(m+1)ss_1..s_m\frac{d^{m+1}}{dx^{m+1}}$ will give

$$1.2..(m+1)ss_1..s_m\frac{d^{m+1}}{dx^{m+1-p}dy^p}$$
$$=\Sigma\left(s\frac{d}{dx}-(m+1)\frac{ds}{dx}\right)..\left(s_{m-p}\frac{d}{dx}-(m-p+1)\frac{ds_{m-p}}{dx}\right)\left(s_{m-p+1}\frac{d}{dy}-(m-p)\frac{ds_{m-p+1}}{dy}\right)..s_m\frac{d}{dy},$$

the y factors being detected at pleasure, provided that they are p in number, and the same factors throughout.

Postscript.

Received March 3, 1860.

In continuing my researches on the extended form of the Index Symbol, I have established a variety of formulæ relative to the case of many variables analogous to those in the case of two. As the expressions occurring in the investigations are frequently of great length, I propose here to give only the principal results, without entering into the details of proof.

Let $i_1, i_2, ..$ be any permutation of the series $1, 2, ..$; and let it be symbolically represented thus:

$$i_1, i_2, .. = \mathrm{P}_i(1, 2, ..).$$

Then any permutation P_j performed on P_i may be similarly represented by $j_{i_1}, j_{i_2}, ..$, or more simply, $ji_1, ji_2, ..$ Then $ji_1, ji_2, ..$ will represent a new permutation of the original series $1, 2, ..$; and the notation above adopted may be extended thus:

$$ji_1, ji_2, .. = \mathrm{P}_{ji}(1, 2, ..)$$
$$\mathrm{P}_j(i_1, i_2, ..) = \mathrm{P}_j\mathrm{P}_i(1, 2, ..),$$

or, dropping the subject of operation,

$$\mathrm{P}_{ji} = \mathrm{P}_j\mathrm{P}_i,$$

and so on generally.

Let there be any number of variables $x_1, x_2, \ldots$, and let

$$\nabla_i = x_{i_1}\frac{d}{dx_1} + x_{i_2}\frac{d}{dx_2} + \ldots$$

$$\nabla_j = x_{j_1}\frac{d}{dx_1} + x_{j_2}\frac{d}{dx_2} + \ldots$$

$$\ldots\ldots\ldots\ldots$$

and $\mathrm{D}_i, \mathrm{D}_j, \ldots$ corresponding expressions when the $\frac{d}{dx_1}, \frac{d}{dx_2}, \ldots$ operate only on some extraneous subject of differentiation, and not on $x_1, x_2, \ldots$ so far as they appear explicitly in the values of $\mathrm{D}_i, \mathrm{D}_j, \ldots$

Then it will be found that

$$\mathrm{D}_j\mathrm{D}_i = \nabla_j\nabla_i - \nabla_{ji}$$

$$\mathrm{D}_k\mathrm{D}_j\mathrm{D}_i = \nabla_j\nabla_k\nabla_i - \nabla_{kj}\nabla_i - \nabla_j\nabla_{ki} - \nabla_k\nabla_{ji} + \nabla_{kji} + \nabla_{jki};$$

and so on for any number of Ds and ∇s. There are special cases in which these expressions take a more symmetrical form. Thus, if the second condition of the system

$$\mathrm{P}(j, k) = \mathrm{P}(k, j), \quad \mathrm{P}(k, i) = \mathrm{P}(i, k), \quad \mathrm{P}(i, j) = \mathrm{P}(j, i)$$

be satisfied, the group $\nabla_{kj}, \nabla_{ki}, \nabla_{ji}$ may be replaced by the group $\nabla_{kj}, \nabla_{ik}, \nabla_{ji}$, in which the suffixes are cyclically arranged. If the first and last are satisfied, the group may be replaced by $\nabla_{ik}, \nabla_{ki}, \nabla_{ij}$. If, besides, the first condition of the system

$$\mathrm{P}\{i(j, k)\} = \mathrm{P}\{(j, k)i\}$$

$$\mathrm{P}\{j(k, i)\} = \mathrm{P}\{(k, i)j\}$$

$$\mathrm{P}\{k(i, j)\} = \mathrm{P}\{(i, j)k\}$$

be satisfied, the expression for $\mathrm{D}_k\mathrm{D}_j\mathrm{D}_i$ may be written

$$\nabla_k\nabla_j\nabla_i - \nabla_i\nabla_{kj} - \nabla_j\nabla_{ik} - \nabla_k\nabla_{ji} + 2\nabla_{kji},$$

or

$$\nabla_k\nabla_j\nabla_i - \nabla_i\nabla_{jk} - \nabla_j\nabla_{ki} - \nabla_k\nabla_{ij} + 2\nabla_{kji},$$

according as the second, or the first and last conditions of the first system are satisfied. And similarly, if the two last conditions of the second system are satisfied, the expression may be written

$$\nabla_k\nabla_j\nabla_i - \nabla_{kj}\nabla_i - \nabla_{ik}\nabla_j - \nabla_{ji}\nabla_k + 2\nabla_{jik}$$

$$\nabla_k\nabla_j\nabla_i - \nabla_{jk}\nabla_i - \nabla_{ki}\nabla_j - \nabla_{ij}\nabla_k + 2\nabla_{jik}.$$

If the accents in the symbols $\nabla_i, \nabla_j, \ldots$ are understood to imply that the suffixes $i, j, \ldots$ and not the ∇s are to be combined, *e. g.*

$$(a, b, c, d)(\nabla_j\nabla_i)^3$$

$$= a\nabla_{jji} + b(\nabla_{jji} + \nabla_{jij} + \nabla_{ijj}) + c(\nabla_{jji} + \nabla_{iji} + \nabla_{jij}) + d\nabla_{jji},$$

then

$$(a, b, c, d)(\mathrm{D}_j, \mathrm{D}_i)^3$$
$$=(a,b,c,d)(\nabla_j,\nabla_i)^3-2(a,b,c,d)(\nabla_j,\nabla_i)(\nabla_j,\nabla_i)^3-(a,b,c,d)(\nabla_j,\nabla_i)^2(\nabla_j,\nabla_i)+2(a,b,c,d)(\nabla_j,\nabla_i)^3,$$

which may be symbolically represented thus:

$$(a, b, c, d)(\mathrm{D}_j, \nabla_i)^3=(a, b, c, d)\begin{vmatrix} (\nabla_j \nabla_i) & 1 & * &) \\ (\nabla_j \nabla_i)^2 & (\nabla_j \nabla_i) & 2 & \\ (\nabla_j \nabla_i)^3 & (\nabla_j \nabla_i)^2 & (\nabla_j \nabla_i) & \end{vmatrix}$$

And generally,

$$(a, b, \ldots)(\ldots \mathrm{D}_j, \nabla_i)^n=(a, b, \ldots)\begin{vmatrix} (\ldots\nabla_j \nabla_i) & 1 & * & \ldots & * &) \\ (\ldots\nabla_j \nabla_i)^2 & (\ldots\nabla_j \nabla_i) & 2 & \ldots & * & \\ (\ldots\nabla_j \nabla_i)^3 & (\ldots\nabla_j \nabla_i)^2 & (\ldots\nabla_j \nabla_i) & \ldots & * & \\ \ldots & \ldots & \ldots & \ldots & \ldots & \\ (\ldots\nabla_j \nabla_i)^n & (\ldots\nabla_j \nabla_i)^{n-1} & (\ldots\nabla_j \nabla_i)^{n-2} & \ldots & (\ldots\nabla_j \nabla_i) & \end{vmatrix}$$

Moreover, if

$$u=\Sigma(1^{a_1} 2^{a_2} \ldots)x_1^{a_1} x_2^{a_2} \ldots$$

Then, understanding that the order of multiplication must be preserved, as in the case of two variables,

$$F(\ldots\nabla_j\nabla_i)u=\Sigma F\Big\{\ldots, \Sigma(\alpha_s+1)\delta^{\frac{d}{dx_s}-\frac{d}{dx_t}}, \quad \Sigma(\alpha_r+1)\delta^{\frac{d}{dx_r}-\frac{d}{dx_t}}\Big\}(1^{a_1} 2^{a_2} \ldots)x_1^{a_1} x_2^{a_2} \ldots$$

Again, if

$$u_{11}=\alpha_{11}x_1+\beta_{11}x_2+\ldots \qquad u_{12}=\alpha_{12}x_1+\beta_{12}x_2\ldots$$
$$u_{21}=\alpha_{21}x_1+\beta_{21}x_2+\ldots \qquad u_{22}=\alpha_{22}x_1+\beta_{22}x_2\ldots$$
$$\ldots\ldots\ldots \qquad \ldots\ldots$$

$$\nabla_1=u_{11}\frac{d}{dx_1}+u_{12}\frac{d}{dx_2}+\ldots$$

$$\nabla_2=u_{21}\frac{d}{dx_1}+u_{22}\frac{d}{dx_2}+\ldots$$

$$\ldots\ldots$$

Then

$$\mathrm{D}_2\mathrm{D}_1=\nabla_2\nabla_1-\Big\{(\alpha_{11}\alpha_{21}+\beta_{11}\alpha_{22}+\ldots)x_1+(\alpha_{11}\beta_{21}+\beta_{11}\beta_{22}+\ldots)x_2+\ldots\Big\}\frac{d}{dx_1}$$
$$-\Big\{(\alpha_{12}\alpha_{21}+\beta_{12}\alpha_{22}+\ldots)x_1+(\alpha_{12}\beta_{21}+\beta_{12}\beta_{22}+\ldots)x_2+\ldots\Big\}\frac{d}{dx_2}$$
$$-\ldots$$

Now the coefficients of the xs are all comprised in the product

$$\left|\begin{matrix} \alpha_{21} & \alpha_{22} & .. \\ \beta_{21} & \beta_{22} & .. \\ . & . & .. \end{matrix}\right| \left\|\begin{matrix} \alpha_{11} & \beta_{11} & .. \\ \alpha_{12} & \beta_{12} & .. \\ . & . & .. \end{matrix}\right|$$

and the terms correspond line for line and column for column. If, therefore,

$$\left|\begin{matrix} a & b & .. \\ a_1 & b_1 & .. \\ . & . & .. \end{matrix}\right| (x, x_1 ..)(y, y_1 ..) = (ax+bx_1+..)y + (a_1x+b_1x_1+..)y_1 + \ldots$$

we may write

$$D_2D_1 = \nabla_2\nabla_1 - \left|\begin{matrix} \alpha_{21} & \beta_{21} & .. \\ \beta_{21} & \beta_{22} & .. \\ . & . & .. \end{matrix}\right| \left\|\begin{matrix} \alpha_{11} & \beta_{11} & .. \\ \alpha_{12} & \beta_{12} & .. \\ . & . & .. \end{matrix}\right| (x_1, x_2, ..)\left(\frac{d}{dx_1}, \frac{d}{dx_2}, ..\right.$$

and by a tolerably obvious extension of the symbolical notation used in other parts of this paper, we may write this expression thus:

$$\nabla_2\nabla_1 - \nabla_2'\nabla_1'.$$

And generally

$$D_nD_{n-1}..D_2\nabla_1 = \left|\begin{matrix} \nabla_n & \nabla_{n-1}' & .. & \nabla_1' \\ \nabla_n' & \nabla_{n-1}' & .. & \nabla_1' \\ . & . & .. & . \\ \nabla_n' & \nabla_{n-1}' & .. & \nabla_1' \end{matrix}\right|$$

Lastly, the formulæ for $ss_1 .. \frac{d^n}{dx^{n-r}dy^r}$ in the case of two variables may be directly extended to the corresponding case of $ss_1 .. \frac{d^n}{dx_1^{a_1}dx_2^{a_2}..}$ with many variables.

III. *On the Resin of* Ficus rubiginosa, *and a new Homologue of Benzylic Alcohol. By* Warren De la Rue, *Ph.D., F.R.S., Treasurer of the Chemical Society, Secretary of the Royal Astronomical Society, &c., and* Hugo Müller, *Ph.D., F.C.S.*

Received December 27, 1859,—Read February 9, 1860.

Among the interesting collection of natural products contributed to the Paris Universal Exhibition of 1855 by the British Colonies, was a gum presenting some remarkable qualities. This substance was stated by the exhibitor to be a new species of gutta percha, in consequence of its becoming plastic when masticated, and on this account it attracted considerable attention. It had been contributed by Dr. Stephenson, of Manning River, N.S.W., who had obtained it from a species of *Ficus*, known as *F. rubiginosa*. The zealous Commissioner for New South Wales, Mr. (now Sir William) M^{c}Arthur, brought this gum under our notice with the view of obtaining some information respecting its chemical properties.

A few preliminary experiments, which were made in Paris, at once showed us that this substance had very little in common with gutta percha, and, moreover, its chemical properties were found to be entirely different from those of that gum. Although our experiments did not allow us to hold out hopes to Mr. M^{c}Arthur of the gum becoming a valuable article of exportation from the colony, they offered some inducement to us to make a more rigorous investigation of it on purely scientific grounds. On communicating this view to Mr. M^{c}Arthur, he liberally placed at our disposal the remainder of the specimen exhibited.

In pursuing subsequently the study of this subject, we discovered one of the proximate constituents to be a Natural Acetic Ether of a new radical homologous to benzyl ($C_{14}H_7$). The peculiar interest which attaches to this class of compounds, induces us to bring under the notice of the Society the results of our investigation.

As the resin under consideration has not, so far as we know, been described, it will not be out of place to commence with an account of its physical characters; we shall next proceed to state the results of our investigation in respect of the chemical characters, first of the gum, then of its constituents. On account of the greater importance of the new Acetic Ether, we shall reserve a description of it until the concluding part of our paper, in order that we may place in immediate juxtaposition an account of the derivatives by which we have been enabled to establish its formula and chemical relations.

This gum or resin exhibits, on the first glance, great similarity in its general appearance to "Gum Euphorbium," occurring, like that substance, in irregular pieces, generally

pierced with holes; some specimens also exhibiting a stalactitic formation. The holes in the fragments of this resin are produced by a small beetle of the tribe "Curculio," which apparently feeds upon, and lives in this resin, as it oozes in a semifluid state from the branch of the tree. We had no means of ascertaining whether or not this insect causes the secretion of the resin by puncturing the branches of the tree, in the same manner as the *Coccus ficus* does for the purpose of depositing its ova. The colour of the gum varies from a dirty yellow or red, almost to white. It is solid and brittle, but some of the larger pieces exhibit, especially in the interior, a degree of toughness which renders it difficult to powder. It is opake, the fracture being dull and wax-like.

At a temperature of about 30° C. (86° Fahr.) this resin becomes soft, when it resembles gutta percha, being plastic without becoming sticky, provided it has been previously wetted with water. In its natural condition this resin possesses neither taste nor odour; but when heated it evolves a wax-like odour, and on being masticated evinces a characteristic taste.

In hot or cold water it is perfectly insoluble, but warm alcohol, ether, oil of turpentine, and other solvents of resinous substances dissolve it with facility. Solutions of caustic alkalies have no effect on it, even when aided by heat.

When left for some time with cold alcohol of ordinary strength, the greater part of the resin is dissolved, whilst a white flocculent substance remains undissolved. By employing this solvent, we succeeded in separating several distinct classes of substances from the Ficus resin. The constituent, readily soluble in cold alcohol, formed an amorphous resinous substance, when separated from the solvent by means of distillation or precipitation with water. The white insoluble part, when further treated with boiling alcohol, is in part dissolved, particles of bark, sand, and other accidental impurities remaining undissolved. The alcoholic solution of the white substance deposits, on cooling, a white crystalline mass, which by repeated crystallization may be obtained in beautiful scaly crystals. From the residue, insoluble in boiling alcohol, bisulphide of carbon or chloroform extract a small quantity of caoutchouc.

A quantitative experiment by the above method yielded the following approximate per-centage result:—

Resinous substance, readily soluble in cold alcohol . . .	73
White crystalline substances, insoluble in cold alcohol, but soluble in warm alcohol	14
Caoutchouc, fragments of bark, sand, and loss	13

The resinous substance, readily soluble in cold alcohol, which forms, according to this analysis, by far the principal constituent of our resin, offered but little inducement for chemical investigation. However, a number of experiments were made, which, although unproductive in their results, may serve to characterize this substance, which possesses peculiarities distinguishing it from other bodies of like origin. In order to identify it hereafter, we propose to call this resin Sycoretin. At the same time we must state that

we were not successful, for reasons hereinafter mentioned, in obtaining this substance perfectly pure.

Sycoretin.

Cold alcohol of moderate strength dissolves the principal part of the original resin, forming a light brown solution, which on precipitation with water, or the separation of the alcohol by means of distillation, furnishes the sycoretin. The alcoholic solution of this resin is perfectly neutral, and scarcely any precipitate is caused in it on the addition of an alcoholic solution of acetate of lead or acetate of copper. This behaviour indicated at once that no acid compounds were present, and that this resin is perfectly neutral. The minute precipitate which formed we ascertained to be tannate of lead, the source of the tannic acid being probably the bark which contaminated the resin. This resin was purified by redissolving it in alcohol, and in order to remove the small amount of colour the solution was treated with animal charcoal, but this had no effect. No better result was obtained when a small quantity of acetate of lead was introduced in the solution, and a basic lead salt thrown down with ammonia. We afterwards found that the colour could be gradually removed by repeated precipitation of the resin from its alcoholic solution by means of water.

The decolorized resin was now redissolved in a just-sufficient quantity of alcohol, and the solution left for some time in a cool place, when a small amount of crystalline substance was deposited, which was filtered off. By the addition of a little water a small quantity of sycoretin was then thrown down, in order to carry down the last traces of the less soluble crystalline compound, in case any were still present. After this treatment the solution was again allowed to stand for some time, but no further precipitate was formed. The clear solution was now partly precipitated with water, and the precipitate removed after it had subsided, heat being used to facilitate the subsidence of the sycoretin by causing the precipitate to agglutinate into one mass. That part of the resin remaining in solution was afterwards thrown down with water and collected separately.

The two different lots of resin thus obtained had the same appearance; both were brittle, but only the last became sticky when masticated, and tasted like the original resin. Both products were powdered and kept for some time *in vacuo* over sulphuric acid, in order to remove all traces of any adhering water or alcohol.

The analysis of the first precipitated part (A) gave the following numbers:—

0·2055 grm. of substance gave 0·5625 grm. carbonic acid, and 0·1870 grm. water.

The analysis of the portion last thrown down (B) gave the following:—

0·1733 grm. of substance gave 0·4950 grm. carbonic acid, and 0·1550 grm. water.

The foregoing results give the following per-centages:—

	A.	B.
Carbon	74·65	77·89
Hydrogen	10·11	9·94

It will be observed from the preceding numbers, that the resin, which has the property of agglutinating on being masticated, is richer in carbon than that first thrown down by water from their alcoholic solution. The peculiar characters of these substances did not, however, permit of any formulæ being determined for them.

Sycoretin is almost white; it is very brittle. It melts in boiling water to a thick liquid, floating on the surface, and when powdered it becomes so electric that it flies out of the mortar. In water, dilute acids, alkaline solutions, or ammonia, it is insoluble; but it is readily soluble in alcohol, ether, chloroform, oil of turpentine, &c.

In order to ascertain whether sycoretin was allied to that class of bodies called glucosides (for example, jalapine), the following experiments were made:—

Action of Sulphuric Acid on Sycoretin.

A portion of the sycoretin, prepared as stated above by fractional precipitation, was added to concentrated sulphuric acid; it was readily dissolved, forming a fine deep red solution, which gave off only a faint odour of sulphurous acid when kept for several days. By exposure to the air, or on addition of water, a brownish precipitate deposited, which differed from the original solution by its lesser solubility; the aqueous liquid contained a trace of a sulpho-copulate acid, but no saccharine substance could be discovered. Treated with a concentrated solution of potash, analogous results were obtained. These experiments show that sycoretin cannot be classed with the glucosides; moreover, all attempts to place this substance in connexion with some of the classified organic compounds were unsuccessful, and we are therefore constrained to leave it for the present among the so-called resins, under which term are comprised all sorts of bodies, acid and neutral, which have nothing in common except some physical resemblance.

Action of Nitric Acid on Sycoretin.

It appears that the only products of the action of concentrated nitric acid are a peculiar nitro-compound and a small quantity of oxalic acid, no picric acid being formed.

On submitting sycoretin to the action of nitric acid, the powdered resin was introduced in small quantities into the acid at the ordinary temperature, and when the action had somewhat subsided, the acid was boiled for some time, when every particle of resin disappeared. The resulting yellow liquid was mixed with water, when a copious precipitate of a pale yellow colour was formed. The precipitate was filtered off, and washed with water. The filtrate, when freed from nitric acid by evaporation, gave an additional precipitate of the nitro-compound on admixture with water. The nitro-compound has slightly acid properties, and is readily soluble in solutions of potash and ammonia. Carbonate of potash also dissolves it, but there is no evolution of carbonic acid, even when the solution is warmed. All the solutions in alkalies are dark yellowish brown, and leave on evaporation an amorphous residue. Lead and other metallic salts give coloured precipitates with its solution, but, as might be expected, no definite compounds

could be procured in this way. The compound with potash, when heated on the platinum-foil, melts, takes fire, puffs up, and burns with the vivacity of other nitro-compounds.

Action of Heat on Sycoretin.

When heated in a retort, sycoretin melts below 100° C. (212° FAHR.), and, at a temperature a few degrees higher, froths considerably, giving off water which retains the peculiar odour perceptible on heating the original resin. On raising the temperature much higher it becomes quiet, and begins to decompose, giving off at first a mobile liquid, and towards the end a dark yellow tar-like substance, leaving only a small quantity of charcoal behind. The distillate so obtained has a disagreeable smell, somewhat like burnt india-rubber; acetic acid being also present in considerable quantity.

Treated with a solution of carbonate of sodium the acetic acid is removed, a dark brown oily liquid remaining, which possesses now a less disagreeable odour. This oily liquid, submitted to a new distillation, gives at first a very fluid liquid, possessing in every respect the properties of caoutchin, and then a thick oily liquid, which soon becomes dark brown when exposed to the air.

Acetate of Sycoceryl.

We assign this name, for reasons hereafter to be mentioned, to the crystallizable substance, which, as already mentioned, is obtained when the residue, left after the treatment of the original resin with cold alcohol, is dissolved in boiling alcohol, and the solution allowed to cool.

For the preparation of this substance the original resin is coarsely powdered and extracted with cold alcohol, in order to remove, as far as possible, the sycoretin. The undissolved residue is then exhausted with boiling alcohol. The several solutions thus obtained are filtered and allowed to cool, when a white deposit is formed, which generally shows but little indication of crystallization. This white deposit is again dissolved in a large quantity of boiling alcohol, and left in a quiet place to cool slowly, when a more perfect crystallization is obtained.

Towards the latter period of the crystallization a substance is deposited of different appearance, being of a more flocculent nature, and altogether different from the crystals first deposited. This substance is present only in a very small quantity, and its separation from the other crystallizable constituents of the resin is attended with great difficulties. In order to effect this separation, the alcoholic solution is allowed to cool to about 40° C. (104° FAHR.), and then the crystals which may have formed are separated by straining off the liquor as quickly as possible through a piece of gauze. The mother-liquor, on further cooling, will now deposit the flocculent substance, contaminated however with the first substance. By repeating this operation a perfect separation of this second substance may be effected.

The crystalline substance (acetate of sycoceryl), by repeated solution in and recrystallization from hot alcohol, was obtained perfectly white and transparent and apparently pure. An examination with the microscope, however, proved that another foreign

body had deposited in smaller crystals on the faces of the supposed pure substance. This new body proved to be much less soluble in different vehicles than our acetate of sycoceryl, but being present only in a very small quantity, its separation caused us at first very great perplexity, but finally we found the following method perfectly efficacious for that purpose.

The dry crystals were placed in a flask, and a quantity of ether insufficient to dissolve the whole substance was introduced, the temperature being maintained at about 30° C. (86° Fahr.); more ether was cautiously added from time to time until the larger crystals had just disappeared, leaving the smaller ones of the new substance undissolved. The separation of the two substances is not, however, perfect in a single operation; for when the flask is allowed to cool, a small part of this parasitical body deposits. After distilling the filtered etheric solution, the acetate of sycoceryl is obtained in a perfect state of purity; and by recrystallization from alcohol, ether or chloroform, it may be procured in beautiful crystals.

Acetate of sycoceryl so obtained is perfectly colourless, and crystallizes from ether in flat prisms, which generally appear as six-sided plates. When crystallized from alcohol the crystals are thin and scaly like mica, and have the greatest resemblance to cholesterin.

Acetate of sycoceryl is brittle, yet difficult to powder, on account of its becoming so very electric when triturated. It melts at 118°—120° C. (244°·4—248° Fahr.), and is still fluid when cooled down to 80° C. (176° Fahr.). It solidifies at first to a transparent mass, which, however, after a short time becomes opake and crystalline, especially if scratched with a hard body. Heated considerably above its melting-point, it boils and distils, almost without decomposition. The distillate is at first liquid, but solidifies after some time, and becomes gradually crystalline. When not perfectly pure, or if the heat is applied too rapidly, it gives out a rancid odour, in which that of acetic acid is recognizable. Hot alcohol, ether, chloroform, benzol, acetone, oil of turpentine, and concentrated acetic acid dissolve the acetate of sycoceryl with great facility. The alcoholic solution is perfectly neutral, and gives no precipitate with alcoholic solutions of the acetates of lead or copper.

Sulphuric acid dissolves it readily, forming a viscid colourless solution, which gets gradually brown, and then gives off traces of sulphurous and acetic acids. When the sulphuric solution is mixed with water, a substance is thrown down which is perfectly hard at common temperatures, but melts below 100° C. (212° Fahr.), and is very difficultly soluble in alcohol, but readily so in chloroform and benzol.

Nitric acid when diluted has no effect, at ordinary temperatures, on acetate of sycoceryl; but if warm, it evolves nitrous fumes, and produces a yellow resinous compound. Fuming nitrous acid, however, dissolves it readily at ordinary temperatures, giving a yellow solution from which water throws down a flocculent amorphous yellow nitro-compound.

Muriatic acid has no effect on acetate of sycoceryl.

Chlorine, bromine, and iodine in contact with this substance act upon it with violence,

especially the two first-named reagents; the products, however, procured in this manner are only resin-like compounds not adapted for analysis.

If, however, a warm alcoholic solution of the acetate of sycoceryl is employed, and the bromine or iodine also added in solution, and in small quantities at a time, the colour of these two reagents disappears, and after cooling a new bromo- or iodo-compound, as the case may be, is deposited in small crystals. The iodine compound is yellow, the bromine compound colourless. The purification of these two promising compounds, and their separation from the unaltered original substances, and another resinous body formed at the same time, was unfortunately not possible with the limited quantity of material which could be devoted to their preparation.

Solution of potash, even when boiled for a long time with the substance under consideration, does not act upon it. If hydrate of potash, however, is melted with it a decomposition takes place, and if the temperature is raised some hydrogen is given off. The product of this reaction, treated with water, leaves behind a colourless amorphous body, which could not be got in a crystalline state, or sufficiently pure for analysis. The alkaline mother-liquor saturated with diluted sulphuric acid became slightly turbid, and the presence of acetic acid was then perceptible. Soda-tartrate of copper gave no reaction indicating the presence of sugar in the solution.

Thus far we did not succeed in producing any derivative which would throw light upon the theoretical composition of our substance, and furnish us with the means of ascertaining its rational formula.

A combustion gave the following numbers:—

I. 0·2745 grm. of substance gave 0·7962 grm. carbonic acid, and 0·2527 grm. water.
II. 0·2649 grm. of substance gave 0·7681 grm. carbonic acid, and 0·2645 grm. water.

These numbers correspond to the following per-centages:—

	I.	II.
Carbon	79·11	79·08
Hydrogen . . .	10·23	10·34

which agree with the empirical formula $C_{20}H_{16}O_2$, our substance being accordingly isomeric with camphor, to which, however, it has no further resemblance.

This composition varies also widely from that of the crystalline substances procured from analogous sources, and which have a great resemblance to our substance; for instance, the crystalline resins on the one hand, Chinese wax and waxes generally on the other.

We have mentioned above, in speaking of the action of various reagents on our new substance, the occurrence of acetic acid under two different circumstances; we did not attach much importance to this fact at the time, because this acid occurs so frequently among the products resulting from the breaking up of organic substances; we nevertheless repeated subsequently these experiments on a somewhat larger scale, with the view, however, chiefly of studying the other products of decomposition which are formed. In order to eliminate as much as possible the effect of temperature, we made use of that

powerful reagent, the so-called "sodium-alcohol," which is obtained by dissolving sodium in absolute alcohol. Sodium-alcohol and potassium-alcohol are at ordinary temperatures generally equivalent in their reactions to the hydrates of those alkalies when in a state of fusion, and hence present the advantage of effecting decompositions in a more simple manner, the effect of a high temperature not interfering with the final result, as is sometimes the case when the fusing hydrated alkalies are employed.

Some experiments of this kind, performed with great care, convinced us that the occurrence of acetic acid could not be attributed to the effect of empyreumatic decomposition, but that it actually existed as an integral proximate constituent of our crystallizable substance. This led us at once to suspect that our substance was in reality an ether-like compound. This supposition was confirmed by the separation of a body which might be considered as the hydrated oxide of a radical; moreover, we were ultimately enabled to give the fullest confirmation to this theoretical speculation, by actually reforming the original substance in a manner suggested by this view.

It should be stated that sodium-alcohol dissolves our substance with the greatest facility, and even at a temperature of 30° C. (86° FAHR.) decomposition takes place, the reaction being unaccompanied by the evolution of gas. On cooling, the solution continues liquid, although a large quantity of the substance may have been employed; but on addition of water, a white flocculent substance separates from the colourless alkaline mother-liquor.

The flocculent substance is insoluble in water, but readily soluble in even cold alcohol. When dissolved in a quantity of boiling alcohol, just sufficient to take it up, the solution on cooling completely solidifies to a mass of beautiful silky crystals, quite different from those of the original substance: this new derivative proved to be the new alcohol which we propose to call Sycocerylic Alcohol.

The aqueous liquor from which the flocculent precipitate was separated remains almost perfectly clear on saturation with a mineral acid; on examination no other product besides a volatile organic acid could be found in it. The existence of a volatile acid with the odour of acetic acid, was rendered evident by saturating the alkaline mother-liquor with phosphoric acid and distilling; the distillate was saturated with carbonate of barium and evaporated to the crystallization point, when prismatic crystals, of the characteristic form of acetate of barium, were obtained. A barium determination gave the following result:—

2·1525 grms. of substance, dried first over sulphuric acid, then at 200° C. (392° FAHR.), gave 1·9593 sulphate of barium, corresponding to 53·52 per cent. barium.

The formula, $C_4H_3BaO_4$, of anhydrous acetate of barium requires 53·73 per cent. of barium.

Alcohol of Sycoceryl.

The preparation of this substance has been already detailed. In order to render it pure, it is only necessary, after it has been precipitated from the solution of sodium alcohol, to wash it well with water in order to remove all traces of fixed alkali; then to crystallize it a few times from warm alcohol. The crystals usually occur aggregated in

spherical masses, like the mineral Wavellite; they are very thin, and have a great resemblance to caffeine.

In several instances during the earlier stages of its purification, or when dilute alcohol is employed for its solution, it was noticed that the substance did not deposit in crystals, but the transparent liquid congealed to a jelly. This jelly, however, after some time became crystalline, the crystallization commencing in several points of the mass, and extending gradually throughout the whole; ultimately a crystallization was obtained of the same appearance as occurs under other circumstances.

In the determination of the rational formula of this substance, we took cognizance of the fact, that, besides acetic acid, it was the only other product obtained in the decomposition of the original compound which we have denominated acetate of sycoceryl, and the analysis of which led to the empirical formula $C_{20}H_{16}O_2$.

From the nature of this compound, we inferred that it contained the radical of acetic acid in a similar state as acetic ether does; that in fact we had to deal with a compound containing acetic acid minus one atom of hydrogen and a radical. According to this view the empirical formula $C_{20}H_{16}O_2$ would have to be doubled, whereby we obtain

$$C_{40}H_{32}O_4;$$

and if we now deduct the elements of acetic acid minus hydrogen $\} = C_4H_3O_4$

we have $C_{36}H_{29}$

for the radical of our new alcohol, whose formula would consequently be $C_{36}H_{30}O_2$.

The analysis of the supposed alcohol obtained from acetate of sycoceryl gave the following results:—

I. 0·1678 grm. of preparation A gave 0·5103 grm. carbonic acid, and 0·1747 grm. water.

II. 0·2547 grm. of preparation B gave 0·7644 grm. carbonic acid, and 0·2568 grm. water.

These numbers correspond to the following per-centages:—

			Analysis.		Mean.
			I.	II.	
C_{36} = 216		82·44	82·94	81·85	82·39
H_{30} = 30		11·45	11·57	11·20	11·38
O_2 = 16		6·11			
262		100·00			

According to this formula our new alcohol would be homologous with benzylic alcohol obtained from "oil of bitter almonds."

Alcohol of sycoceryl is perfectly insoluble in water, the fixed alkalies, and ammonia; but alcohol, especially when warm, also ether, benzol, chloroform, and naphtha, are good solvents for it.

At a temperature of about 90° C. (194° FAHR.), sycocerylic alcohol melts to a liquid heavier than water, and solidifies on cooling to a crystalline mass, especially if any

fragments of crystals have remained unfused, because they become the foci of a new crystallization. When, however, the heat is increased only a little beyond the fusion-point, it remains perfectly transparent and amorphous. By contact with alcohol, this glassy condition is changed to the normal crystalline structure. Heated considerably above its melting-point, a portion distils unchanged, and there remains a brownish residue in the retort.

Potassium brought in contact with this substance when in a state of fusion disengages hydrogen, and becomes covered with a white crust; but when heat is applied in order to fuse the so-formed potassium-compound of the sycocerylic alcohol, the reaction becomes so violent that the mass blackens and even catches fire.

Heated with hydrate of potash above the melting-point of the latter, it evolves hydrogen and becomes decomposed; it appears that this reaction does not stop with the probable formation of an acid which unites with the potash, but goes further, for in the product of this reaction we did not find the expected acid; but it is our intention to pursue this subject if ever we are so fortunate as to procure a larger supply of material.

Concentrated sulphuric acid dissolves readily sycocerylic alcohol with evolution of heat, forming a brown liquid which remains unaltered for some time. The liquid yields, on addition of water, a resinous viscid substance which melts at the temperature of boiling water, and is but very sparingly soluble in alcohol. Ether and chloroform dissolve it with facility, and, on evaporating, merely leave the resinous product in its original amorphous state. The aqueous liquor, saturated with carbonate of barium, gave no indications of the presence of a conjugated sulphuric acid.

Chlorine, bromine, and iodine act readily on sycocerylic alcohol: if solutions of these reagents are used, crystalline compounds are formed. The iodine compound is of a yellow colour.

In one experiment we obtained, on acting with sodium-alcohol on acetate of sycoceryl, a substance which resembled the alcohol just described, and which gave, on burning, the following numbers:—

I. 0·2873 grm. of substance gave 0·8885 grm. carbonic acid, and 0·3042 grm. water.

II. 0·1887 grm. of substance gave 0·5843 grm. carbonic acid, and 0·2017 grm. water.

The per-centage derived from these results agrees nearly with the composition of the ether of sycoceryl, $C_{72}H_{58}O_4$, which might be formed under favourable conditions. This formula would require the following numbers:—

		Analysis.	
		I.	II.
$C_{72}=432$	85·376	84·81	84·5
$H_{58}=58$	11·462	11·76	11·87
$O_4=16$	3·162		
506	100·000		

Action of Chloride of Phosphorus on Sycocerylic Alcohol.

For the purpose of preparing the chloride of sycoceryl, we employed pentachloride of phosphorus and a solution of sycocerylic alcohol in benzol. At common temperatures no reaction took place, but when the temperature was elevated to about 60° C. (140° Fahr.), hydrochloric acid was given off, and the pentachloride gradually disappeared. After the disengagement of hydrochloric acid had ceased, the liquid was removed from the remaining pentachloride and washed with water, and afterwards with an alkaline solution. After the benzol had been got rid of by keeping the liquid for some time in a warm place, a viscid residue was obtained, which was soluble with great difficulty in alcohol, but easily soluble in ether or chloroform. These solutions, after evaporation, deposited this substance again in its original sticky state. In the first experiments, which were carried out only on a very small scale, a crystalline substance was formed besides the amorphous greenish compound. This crystalline substance differed in its properties from the original alcohol. It therefore seems probable that a slight excess of pentachloride (or the phosphoric acid formed during the reaction) destroys to a great extent the chloride of sycoceryl formed during the reaction; or at all events, phosphate of sycoceryl, which is produced simultaneously and predominates, cannot be separated from the chloride. We are therefore at present unable to give a description of the chloride of sycoceryl in its pure state.

Benzoate of Sycoceryl.

Chloride of benzoyl dissolves with the greatest facility a large quantity of sycocerylic alcohol at common temperatures, but no hydrochloric acid is disengaged; probably, therefore, no reaction takes place at ordinary temperatures, but if heat is applied the liquid soon commences to give off hydrochloric acid. When the evolution of hydrochloric acid has ceased, the mixture is allowed to cool, when it solidifies to a fibrous crystalline mass. Any excess of chloride of benzoyl is removed after the reaction by throwing the mixture into a solution of bicarbonate of potassium, whereby a resinous mass separates. The whole being kept warm for several hours, all the chloride of benzoyl is decomposed. During this process a slight smell, somewhat like benzoate of ethyl, is perceptible. The resinous mass, after removal from the saline liquors, is washed several times with warm water; it is now free from benzoic acid and chloride of benzoyl. On boiling the resinous mass with absolute alcohol, a trace of a yellowish secondary product dissolves, leaving the principal quantity undissolved, which then appears as a white crystalline mass.

The product thus obtained, on being boiled with a large quantity of ether, and the solution allowed to cool, is procured in small crystals, which are soluble with difficulty in ether. Absolute alcohol dissolves only a trace of this substance, and when boiled with it deposits the dissolved part on cooling in minute spherical aggregations of crystals, which under the microscope are seen to be prismatic.

The best solvent for this compound is benzol, it being soluble in all proportions in this liquid. On evaporating the solution, the substance is left behind in fine prismatic crystals. Chloroform behaves like benzol; but the crystals obtained from this solvent are much finer, and can be obtained of considerable size.

In order to ascertain the nature of the compound produced by the action of chloride of benzoyl on sycocerylic alcohol, we decomposed it by means of sodium-alcohol, which we found to be preferable to any other form of caustic alkali. Even with this reagent the decomposition is effected only with difficulty; possibly on account of the new substance being only sparingly soluble, and also on account of the benzoate of sodium which results not being much more soluble in the alcohol. However, after boiling for some time, the benzoate of sycoceryl disappears. On addition of water a voluminous substance was separated, which proved to be the regenerated alcohol of sycoceryl.

The aqueous liquid saturated with an acid soon formed a crystalline precipitate, which, on removal with ether, proved to be benzoic acid.

The foregoing experiments bear conclusive evidence that the alcohol of sycoceryl behaves toward chloride of benzoyl in a manner perfectly analogous with that of other members of the alcoholic group, that is to say, a benzoate of the ether radical being formed.

After having shown that the substance separated by sodium-alcohol may be regarded as the alcohol of the new radical sycoceryl, it became desirable to have a synthetic proof of this theory; and it occurred to us that if we could succeed in combining the sycocerylic alcohol again with the radical of othyl (acetyl), and thus reproduce the original substance, which we have called acetate of sycoceryl, it would be the best possible confirmation of our views. In order to test this, we accordingly brought chloride of othyl (acetyl) in contact with sycocerylic alcohol. At ordinary temperatures no action took place; but when a little heat was applied the alcohol was dissolved, and the liquid commenced to boil, giving off copious fumes of hydrochloric acid. After the reaction had ceased heat was again applied, and the whole subjected to the boiling temperature for some time, in order to get rid of the excess of othyl. After cooling, the resulting product was boiled with water, when a heavy oily body separated. The boiling with water was continued for some time, until at last the oily liquid became perfectly solid and beautifully crystalline; indicating at once that a substance had been formed differing from the original alcohol, which, it will be remembered, is fluid at the temperature of boiling water.

This white crystalline substance was now dissolved in boiling alcohol, of which it required a considerable quantity, and subsequently allowed to cool. When almost the whole had dissolved a small quantity of a compound was left behind, which at last melted, being evidently a new substance, the probable product of the action of a small quantity of oxychloride of phosphorus which contaminated the chloride of othyl.

On cooling, the filtered liquid commenced to crystallize, yielding beautiful iridescent flat prismatic crystals, which sparkled with the colours of the rainbow in the solution,

like chlorate of potash does in the act of crystallizing. The crystallized substance produced in this experiment proved to be in every respect identical with the natural acetate of sycoceryl, and thus gave the most direct confirmation to our theoretical views.

Having thus established the nature of the sycocerylic alcohol, it became desirable to produce also the acid which would be homologous with benzoic acid, and would stand in regard to this acid in such a relation as palmitic acid does to the lower members of the series to which it belongs. A small quantity of the alcohol was therefore boiled for about six hours with dilute nitric acid. A feeble reaction was indicated by the slight evolution of nitrous fumes, and after some time the sycocerylic alcohol became of a dark yellow colour, and presented a resinous aspect. After digesting for six hours, the resinous product was removed, washed with water, and dried. This substance was readily soluble in warm alcohol, and on cooling a white crystalline substance was deposited.

This crystalline substance had all the characters of an acid; it was perfectly soluble in an aqueous solution of potash or ammonia, and gave with an alcoholic solution of acetate of lead a copious precipitate. Although this reaction showed that we had obtained an acid which possesses all the properties that might be anticipated of an acid corresponding to our alcohol, we could not, with the very small quantity of substance at our disposal, get enough of it in a pure state for analysis, on account of the yellow nitro-compound (apparently the nitro-acid of the new acid) adhering with great obstinacy to it, and accompanying it in all its compounds and solutions. In order to exclude the formation of this secondary product, we tried the action of chromic acid on sycocerylic alcohol; a small quantity of the alcohol was boiled with a moderately concentrated solution of chromic acid for about eight hours. The product so obtained was washed and boiled with a dilute solution of potash, but after saturating this alkaline solution with an acid, no precipitate was formed, and it was altogether impossible to detect any acid; therefore we must conclude that this acid was not formed by this treatment.

On one occasion, on repeating this experiment, we accidentally observed, among the products of the action of chromic acid on sycocerylic alcohol, a crystalline body; on treating the mass with dilute alcohol, this product was procured in large flat prisms, resembling somewhat in appearance acetate of sycoceryl, but differing in its melting-point, and was perfectly neutral. From the mode of formation, it might be inferred that we had obtained the aldehyde ($C_{26}H_{28}O_2$) corresponding to our alcohol, but the minuteness of the quantity procured rendered it impossible to decide this point.

For the present we must content ourselves with the foregoing account of the compounds of the radical sycoceryl, the very small amount of the substance at our disposal being barely sufficient for the performance of those experiments which we have described.

The great interest which naturally attaches to this new homologue of the benzyl-alcohol series will be a sufficient inducement for us to take up this subject again, for the purpose of studying its derivatives, should we be so fortunate as to obtain a further supply of raw material.

On reviewing the members of which benzylic alcohol of CANNIZZARO is the type, and with which our new alcohol must be classed, it will be perceived that there are still many gaps to be filled up in their series.

Benzylic alcohol (Kresylic alcohol, Taurylic alcohol)	$C_{14}H_8O_2$	
	$C_{16}H_{10}O_2$	unknown.
	$C_{18}H_{12}O_2$	
Cuminylic alcohol (Thymol and Carvacrol) . . .	$C_{20}H_{14}O_2$	
	$C_{22}H_{16}O_2$	
	$C_{24}H_{18}O_2$	
	$C_{26}H_{20}O_2$	
	$C_{28}H_{22}O_2$	unknown.
	$C_{30}H_{24}O_2$	
	$C_{32}H_{26}O_2$	
	$C_{34}H_{28}O_2$	
Sycocerylic alcohol	$C_{26}H_{30}O_2$	

On comparing the properties of our sycocerylic alcohol with those of benzylic alcohol, very little resemblance will at first be traceable between them; but when it is remembered that there are not fewer than ten steps between benzylic and sycocerylic alcohol, this difference of properties is easily accounted for; more particularly if we take into consideration a similar case in another homologous series, the links of which are more fully known. The change in the properties of the acetic acid series, for example, by each increment of increase of C_2H_2, is quite as remarkable; and when we compare acetic acid on the one hand with palmitic acid on the other, the dissimilarity is not less remarkable than if we compare sycocerylic alcohol, $C_{26}H_{30}O_2$, with benzylic alcohol, $C_{14}H_8O_2$.

In conclusion, we may mention that benzylic alcohol, and consequently also cuminylic alcohol, are generally considered to be homologues of phenyl-alcohol (carbolic acid); kresyl-alcohol would be isomeric with benzyl-alcohol, and carvacrol and thymol with cuminylic alcohol. On comparing these substances we find that this view is not tenable, and that there exist in reality at least two distinct series of isomeric compounds, the types of which are benzylic alcohol on the one hand and phenylic alcohol on the other.

The crystalline substance which adhered to the acetate of sycoceryl, and which it will be recollected was left in part undissolved when the acetate was dissolved out with ether, can be obtained in only very small crystals. It is perfectly neutral, and we did not succeed in obtaining any derivative from it calculated to throw light on its true nature. The quantity was indeed extremely small, and we therefore content ourselves with giving the ultimate analysis of it.

0·1806 grm. substance gave 0·5070 grm. carbonic acid, and 0·2000 water.

These numbers give the following per-centage:—carbon 76·56, hydrogen 12·30.

IV. *On the Theory of Compound Colours, and the Relations of the Colours of the Spectrum.*

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Received January 5,—Read March 22, 1860.

§ I. *Introduction.*

According to Newton's analysis of light*, every colour in nature is produced by the mixture, in various proportions, of the different kinds of light into which white light is divided by refraction. By means of a prism we may analyse any coloured light, and determine the proportions in which the different homogeneous rays enter into it; and by means of a lens we may recombine these rays, and reproduce the original coloured light.

Newton has also shown† how to combine the different rays of the spectrum so as to form a single beam of light, and how to alter the proportions of the different colours so as to exhibit the result of combining them in any arbitrary manner.

The number of different kinds of homogeneous light being infinite, and the proportion in which each may be combined being also variable indefinitely, the results of such combinations could not be appreciated by the eye, unless the chromatic effect of every mixture, however complicated, could be expressed in some simpler form. Colours, as seen by the human eye of the normal type, can all be reduced to a few classes, and expressed by a few well-known names; and even those colours which have different names have obvious relations among themselves. Every colour, except purple, is similar to some colour of the spectrum‡, although less intense; and all purples may be compounded of blue and red, and diluted with white to any required tint. Brown colours, which at first sight seem different, are merely red, orange or yellow of feeble intensity, more or less diluted with white.

It appears therefore that the result of any mixture of colours, however complicated, may be defined by its relation to a certain small number of well-known colours. Having selected our standard colours, and determined the relations of a given colour to these, we have defined that colour completely as to its appearance. Any colour which has the same relation to the standard colours, will be identical in appearance, though its optical constitution, as revealed by the prism, may be very different.

* Optics, book i. part 2. prop. 7.

† Lectiones Opticæ, part 2. § 1. p. 100 to 105; and Optics, book i. part 2. prop. 11.

‡ Optics, book i. part 2. prop. 4.

We may express this by saying that two compound colours may be *chromatically* identical, but *optically* different. The *optical* properties of light are those which have reference to its origin and propagation through media, till it falls on the sensitive organ of vision; the *chromatical* properties of light are those which have reference to its power of exciting certain sensations of *colour*, perceived through the organ of vision.

The investigation of the chromatic relations of the rays of the spectrum must therefore be founded upon observations of the apparent identity of compound colours, as seen by an eye either of the normal or of some abnormal type; and the results to which the investigation leads must be regarded as partaking of a physiological, as well as of a physical character, and as indicating certain laws of sensation, depending on the constitution of the organ of vision, which may be different in different individuals. We have to determine the laws of the composition of colours in general, to reduce the number of standard colours to the smallest possible, to discover, if we can, what they are, and to ascertain the relation which the homogeneous light of different parts of the spectrum bears to the standard colours.

§ II. *History of the Theory of Compound Colours.*

The foundation of the theory of the composition of colours was laid by NEWTON*. He first shows that, by the mixture of homogeneal light, colours may be produced which are "like to the colours of homogeneal light as to the appearance of colour, but not as to the immutability of colour and constitution of light." Red and yellow give an orange colour, which is chromatically similar to the orange of the spectrum, but optically different, because it is resolved into its component colours by a prism, while the orange of the spectrum remains unchanged. When the colours to be mixed lie at a distance from one another in the spectrum, the resultant appears paler than that intermediate colour of the spectrum which it most resembles; and when several are mixed, the resultant may appear white. NEWTON† is always careful, however, not to call any mixture white, unless it agrees with common white light in its optical as well as its chromatical properties, and is a mixture of *all* the homogeneal colours. The theory of compound colours is first presented in a mathematical form in prop. 6, "*In a mixture of primary colours, the quantity and quality of each being given, to know the colour of the compound.*" He divides the circumference of a circle into seven parts, proportional to the seven musical intervals, in accordance with his opinion about the proportions of the colours in the spectrum. At the centre of gravity of each of these arcs he places a little circle, whose area is proportional to the number of rays of the corresponding colour which enter into the given mixture. The position of the centre of gravity of all these circles indicates the nature of the resultant colour. A radius drawn through it points out that colour of the spectrum which it most resembles, and the distance from the centre determines the fulness of its colour.

With respect to this construction, NEWTON says, "This rule I conceive accurate enough

* Optics, book i. part 2. props. 4, 5, 6.

† 7th and 8th Letters to Oldenburg.

for practice, though not mathematically accurate." He gives no reasons for the different parts of his rule, but we shall find that his method of finding the centre of gravity of the component colours is completely confirmed by my observations, and that it involves mathematically the theory of three elements of colour; but that the disposition of the colours on the circumference of a circle was only a provisional arrangement, and that the true relations of the colours of the spectrum can only be determined by direct observation.

YOUNG* appears to have originated the theory, that the three elements of colour are determined as much by the constitution of the sense of sight as by anything external to us. He conceives that three different sensations may be excited by light, but that the proportion in which each of the three is excited depends on the nature of the light. He conjectures that these primary sensations correspond to red, green, and violet. A blue ray, for example, though homogeneous in itself, he conceives capable of exciting both the green and the violet sensation, and therefore he would call blue a compound colour, though the colour of a simple kind of light. The *quality* of any colour depends, according to this theory, on the *ratios* of the intensities of the three sensations which it excites, and its *brightness* depends on the *sum* of these three intensities.

Sir DAVID BREWSTER, in his paper entitled "On a New Analysis of Solar Light, indicating three Primary Colours, forming Coincident Spectra of equal length†," regards the actual colours of the spectrum as arising from the intermixture, in various proportions, of three primary kinds of light, red, yellow, and blue, each of which is variable in intensity, but uniform in colour, from one end of the spectrum to the other; so that every colour in the spectrum is really compound, and might be shown to be so if we had the means of separating its elements.

Sir DAVID BREWSTER, in his researches, employed coloured media, which, according to him, absorb the three elements of a single prismatic colour in different degrees, and change their proportions, so as to alter the colour of the light, without altering its refrangibility.

In this paper I shall not enter into the very important questions affecting the physical theory of light, which can only be settled by a careful inquiry into the phenomena of absorption. The physiological facts, that we have a threefold sensation of colour, and that the three elements of this sensation are affected in different proportions by light of different refrangibilities, are equally true, whether we adopt the physical theory that there are three kinds of light corresponding to these three colour-sensations, or whether we regard light of definite refrangibility as an undulation of known length, and therefore variable only in intensity, but capable of producing different chemical actions on different substances, of being absorbed in different degrees by different media, and of exciting in different degrees the three different colour-sensations of the human eye.

* YOUNG's Lectures on Natural Philosophy, KELLAND's Edition, p. 345, or Quarto, 1807, vol. i. p. 441 see also YOUNG in Philosophical Transactions, 1801, or Works in Quarto, vol. ii. p. 617.

† Transactions of the Royal Society of Edinburgh, vol. xii. p. 123.

Sir DAVID BREWSTER has given a diagram of three curves, in which the base-line represents the length of the spectrum, and the ordinates of the curves represent, by estimation, the intensities of the three kinds of light at each point of the spectrum. I have employed a diagram of the same kind to express the results arrived at in this paper, the ordinates being made to represent the intensities of each of the three elements of colour, as calculated from the experiments.

The most complete series of experiments on the mixture of the colours of the spectrum, is that of Professor HELMHOLTZ* of Königsberg. By using two slits at right angles to one another, he formed two pure spectra, the fixed lines of which were seen crossing one another when viewed in the ordinary way by means of a telescope. The colours of these spectra were thus combined in every possible way, and the effect of the combination of any two could be seen separately by drawing the eye back from the eyepiece of the telescope, when the compound colour was seen by itself at the eye-hole. The proportion of the components was altered by turning the combined slits round in their own plane.

One result of these experiments was, that a colour, chromatically identical with white, could be formed by combining yellow with indigo. M. HELMHOLTZ was not then able to produce white with any other pair of simple colours, and considered that three simple colours were required in general to produce white, one from each of the three portions into which the spectrum is divided by the yellow and indigo.

Professor GRASSMANN† showed that NEWTON'S theory of compound colours implies that there are an infinite number of pairs of complementary colours in the spectrum, and pointed out the means of finding them. He also showed how colours may be represented by lines, and combined by the method of the parallelogram.

In a second memoir‡, M. HELMHOLTZ describes his method of ascertaining these pairs of complementary colours. He formed a pure spectrum by means of a slit, a prism, and a lens; and in this spectrum he placed an apparatus having two parallel slits which were capable of adjustment both in position and breadth, so as to let through any two portions of the spectrum, in any proportions. Behind this slit, these rays were united in an image of the prism, which was received on paper. By arranging the slits, the colour of this image may be reduced to white, and made identical with that of paper illuminated with white light. The wave-lengths of the component colours were then measured by observing the angle of diffraction through a grating. It was found that the colours from red to green-yellow ($\lambda=2082$) were complementary to colours ranging from green-blue ($\lambda=1818$) to violet, and that the colours between green-yellow and green-blue have no homogeneous complementaries, but must be neutralized by mixtures of red and violet.

M. HELMHOLTZ also gives a provisional diagram of the curve formed by the spectrum on NEWTON'S diagram, for which his experiments did not furnish him with the complete data.

* POGGENDORFF'S Annalen, Band lxxxvii. (Philosophical Magazine, 1852, December.)

† POGGENDORFF'S Annalen, Band lxxxix. (Philosophical Magazine, 1854, April.) ‡ Ibid. Band xciv.

Accounts of experiments by myself on the mixture of artificial colours by rapid rotation, may be found in the Transactions of the Royal Society of Edinburgh, vol. xxi. pt. 2 (1855); in an appendix to Professor George Wilson's work on Colour-Blindness; in the Report of the British Association for 1856, p. 12; and in the Philosophical Magazine, July 1857, p. 40. These experiments show that, for the normal eye, there are three, and only three, elements of colour, and that in the colour-blind one of these is absent. They also prove that chromatic observations may be made, both by normal and abnormal eyes, with such accuracy, as to warrant the employment of the results in the calculation of colour-equations, and in laying down colour-diagrams by Newton's rule.

The first instrument which I made (in 1852) to examine the mixtures of the colours of the spectrum was similar to that which I now use, but smaller, and it had no constant light for a term of comparison. The second was $6\frac{1}{2}$ feet long, made in 1855, and showed *two* combinations of colour side by side. I have now succeeded in making the mixture much more perfect, and the comparisons more exact, by using white reflected light, instead of the second compound colour. An apparatus in which the light passes through the prisms, and is reflected back again in nearly the same path by a concave mirror, was shown by me to the British Association in 1856. It has the advantage of being portable, and need not be more than half the length of the other, in order to produce a spectrum of equal length. I am so well satisfied with the working of this form of the instrument, that I intend to make use of it in obtaining equations from a greater variety of observers than I could meet with when I was obliged to use the more bulky instrument. It is difficult at first to get the observer to believe that the compound light can ever be so adjusted as to appear to his eyes identical with the white light in contact with it. He has to learn what adjustments are necessary to produce the requisite alteration under all circumstances, and he must never be satisfied till the two parts of the field are identical in colour and illumination. To do this thoroughly, implies not merely good eyes, but a power of judging as to the exact nature of the difference between two very pale and nearly identical tints, whether they differ in the amount of red, green, or blue, or in brightness of illumination.

In the following paper I shall first lay down the mathematical theory of Newton's diagram, with its relation to Young's theory of the colour-sensation. I shall then describe the experimental method of mixing the colours of the spectrum, and determining the wave-lengths of the colours mixed. The results of my experiments will then be given, and the chromatic relations of the spectrum exhibited in a system of colour-equations, in Newton's diagram, and in three curves of intensity, as in Brewster's diagram. The differences between the results of two observers will then be discussed, showing on what they depend, and in what way such differences may affect the vision of persons otherwise free from defects of sight.

§ III. *Mathematical Theory of* NEWTON'S *Diagram of Colours.*

NEWTON'S diagram is a plane figure, designed to exhibit the relations of colours to each other.

Every point in the diagram represents a colour, simple or compound, and we may conceive the diagram itself so painted, that every colour is found at its corresponding point. Any colour, differing only in quantity of illumination from one of the colours of the diagram, is referred to it as a unit, and is measured by the ratio of the illumination of the given colour to that of the corresponding colour in the diagram. In this way the *quantity* of a colour is estimated. The resultant of mixing any two colours of the diagram is found by dividing the line joining them inversely as the quantity of each; then, if the sum of these quantities is unity, the resultant will have the illumination as well as the colour of the point so found; but if the sum of the components is different from unity, the *quantity* of the resultant will be measured by the sum of the components.

This method of determining the position of the resultant colour is mathematically identical with that of finding the centre of gravity of two weights, and placing a weight equal to their sum at the point so found. We shall therefore speak of the resultant tint as the sum of its components placed at their centre of gravity.

By compounding this resultant tint with some other colour, we may find the position of a mixture of three colours, at the centre of gravity of its components; and by taking these components in different proportions, we may obtain colours corresponding to every part of the triangle of which they are the angular points. In this way, by taking any three colours we should be able to construct a triangular portion of NEWTON'S diagram by painting it with mixtures of the three colours. Of course these mixtures must be made to correspond with optical mixtures of light, not with mechanical mixtures of pigments.

Let us now take any colour belonging to a point of the diagram outside this triangle. To make the centre of gravity of the three weights coincide with this point, one or more of the weights must be made negative. This, though following from mathematical principles, is not capable of direct physical interpretation, as we cannot exhibit a negative colour.

The equation between the three selected colours, x, y, z, and the new colour u, may in the first case be written

$$u=x+y+z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

x, y, z being the quantities of colour required to produce u. In the second case suppose that z must be made negative,

$$u=x+y-z. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

As we cannot realize the term $-z$ as a negative colour, we transpose it to the other side of the equation, which then becomes

$$u+z=x+y, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

which may be interpreted to mean, that the resultant tint, $u+z$, is identical with the resultant, $x+y$. We thus find a mixture of the new colour with one of the selected colours, which is chromatically equivalent to a mixture of the other two selected colours.

When the equation takes the form

$$u=x-y-z, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

two of the components being negative, we must transpose them thus,

$$u+y+z=x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

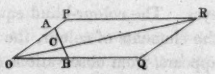
which means that a mixture of certain proportions of the new colour and two of the three selected, is chromatically equivalent to the third. We may thus in all cases find the relation between any three colours and a fourth, and exhibit this relation in a form capable of experimental verification; and by proceeding in this way we may map out the positions of all colours upon NEWTON's diagram. Every colour in nature will then be defined by the position of the corresponding colour in the diagram, and by the ratio of its illumination to that of the colour in the diagram.

§ IV. *Method of representing Colours by Straight Lines drawn from a Point.*

To extend our ideas of the relations of colours, let us form a new geometrical conception by the aid of solid geometry.

Let us take as origin any point not in the plane of the diagram, and let us draw lines through this point to the different points of the diagram; then the direction of any of these lines will depend upon the position of the point of the diagram through which it passes, so that we may take this line as the representative of the corresponding colour on the diagram.

In order to indicate the *quantity* of this colour, let it be produced beyond the plane of the diagram in the same ratio as the given colour exceeds in illumination the colour on the diagram. In this way every colour in nature will be represented by a line drawn through the origin, whose *direction* indicates the *quality* of the colour, while its *length* indicates its *quantity*.



Let us find the resultant of two colours by this method. Let O be the origin and AB be a section of the plane of the diagram by that of the paper. Let OP, OQ be lines representing colours, A, B the corresponding points in the diagram; then the quantity of P will be $\frac{OP}{OA}=p$, and that of Q will be $\frac{OQ}{OB}=q$. The resultant of these will be represented in the diagram by the point C, where $AC:CB::q:p$, and the quantity of the resultant will be $p+q$, so that if we produce OC to R, so that $OR=(p+q)OC$, the line OR will represent the resultant of OP and OQ in direction and magnitude. It is easy to prove, from this construction, that OR is the diagonal of the parallelogram of which OP and OQ are two sides. It appears therefore that if colours are represented in quantity and quality by the magnitude and direction of straight lines, the rule for the composition of colours is identical with that for the composition of forces in mechanics. This analogy has been well brought out by Professor GRASSMANN in POGGENDORFF's 'Annalen,' Bd. lxxxix.

We may conceive an arrangement of actual colours in space founded upon this construction. Suppose each of these radiating lines representing a given colour to be itself illuminated with that colour, the brightness increasing from zero at the origin to unity, where it cuts the plane of the diagram, and becoming continually more intense in proportion to the distance from the origin. In this way every colour in nature may be matched, both in quality and quantity, by some point in this coloured space.

If we take any three lines through the origin as axes, we may, by coordinates parallel to these lines, express the position of any point in space. That point will correspond to a colour which is the resultant of the three colours represented by the three coordinates.

This system of coordinates is an illustration of the resolution of a colour into three components. According to the theory of YOUNG, the human eye is capable of three distinct primitive sensations of colour, which, by their composition in various proportions, produce the sensations of actual colour in all their varieties. Whether any kinds of light have the power of exciting these primitive sensations separately, has not yet been determined.

If colours corresponding to the three primitive sensations can be exhibited, then all colours, whether produced by light, disease, or imagination, are compounded of these, and have their places within the triangle formed by joining the three primaries. If the colours of the pure spectrum, as laid down on the diagram, form a triangle, the colours at the angles *may* correspond to the primitive sensations. If the curve of the spectrum does not reach the angles of the circumscribing triangle, then no colour in the spectrum, and therefore no colour in nature, corresponds to any of the three primary sensations.

The only data at present existing for determining the primary colours, are derived from the comparison of observations of colour-equations by colour-blind, and by normal eyes. The colour-blind equations differ from the others by the non-existence of one of the elements of colour, the relation of which to known colours can be ascertained. It appears, from observations made for me by two colour-blind persons*, that the elementary sensation which they do not possess is a red approaching to crimson, lying beyond both vermilion and carmine. These observations are confirmed by those of Mr. POLE, and by others which I have obtained since. I have hopes of being able to procure a set of colour-blind equations between the colours of the spectrum, which will indicate the missing primary in a more exact manner.

The experiments which I am going to describe have for their object the determination of the position of the colours of the spectrum upon NEWTON'S diagram, from actual observations of the mixtures of those colours. They were conducted in such a way, that in every observation the judgment of the observer was exercised upon two parts of an illuminated field, one of which was so adjusted as to be chromatically identical with the other, which, during the whole series of observations, remained of one constant

* Transactions of the Royal Society of Edinburgh, vol. xxi. pt. 2. p. 286.

intensity of white. In this way the effects of subjective colours were entirely got rid of, and all the observations were of the same kind, and therefore may claim to be equally accurate; which is not the case when comparisons are made between bright colours of different kinds.

The chart of the spectrum, deduced from these observations, exhibits the colours arranged very exactly along two sides of a triangle, the extreme red and violet forming doubtful portions of the third side. This result greatly simplifies the theory of colour, if it does not actually point out the three primary colours themselves.

§ V. *Description of an Instrument for making definite Mixtures of the Colours of the Spectrum.*

The experimental method which I have used consists in forming a combination of three colours belonging to different portions of the spectrum, the quantity of each being so adjusted that the mixture shall be white, and equal in intensity to a given white. Fig. 1, Plate I. represents the instrument for making the observations. It consists of two tubes, or long boxes, of deal, of rectangular section, joined together at an angle of about 100°.

The part AK is about 5 feet long, 7 inches broad, and 4 deep; KN is about 2 feet long, 5 inches broad, and 4 deep; BD is a partition parallel to the side of the long box. The whole of the inside of the instrument is painted black, and the only openings are at the end AC, and at E. At the angle there is a lid, which is opened when the optical parts have to be adjusted or cleaned.

At E is a fine vertical slit; L is a lens; at P there are two equilateral prisms. The slit E, the lens L, and the prisms P are so adjusted, that when light is admitted at E a *pure spectrum* is formed at AB, the extremity of the long box. A mirror at M is also adjusted so as to reflect the light from E along the narrow compartment of the long box to BC. See fig. 3.

At AB is placed the contrivance shown in fig. 2, Plate I. A′B′ is a rectangular frame of brass, having a rectangular aperture of 6×1 inches. On this frame are placed six brass sliders, XYZ. Each of these carries a knife-edge of brass in the plane of the surface of the frame.

These six moveable knife-edges form three slits, XYZ, which may be so adjusted as to coincide with any three portions of the pure spectrum formed by light from E. The intervals behind the sliders are closed by hinged shutters, which allow the sliders to move without letting light pass between them.

The inner edge of the brass frame is graduated to twentieths of an inch, so that the position of any slit can be read off. The breadth of the slit is ascertained by means of a wedge-shaped piece of metal, 6 inches long, and tapering to a point from a breadth of half an inch. This is gently inserted into each slit, and the breadth is determined by the distance to which it enters, the divisions on the wedge corresponding to the 200th of an inch difference in breadth, so that the unit of breadth is ·005 inch.

Now suppose light to enter at E, to pass through the lens, and to be refracted by the two prisms at P; a pure spectrum, showing FRAUNHOFER'S lines, is formed at AB, but only that part is allowed to pass which falls on the three slits XYZ. The rest is stopped by the shutters. Suppose that the portion falling on X belongs to the red part of the spectrum; then, of the white light entering at E, only the red will come through the slit X. If we were to admit red light at X it would be refracted to E, by the principle in Optics, that the course of any ray may be reversed. If, instead of red light, we were to admit white light at X, still only red light would come to E; for all other light would be either more or less refracted, and would not reach the slit at E. Applying the eye at the slit E, we should see the prism P uniformly illuminated with red light, of the kind corresponding to the part of the spectrum which falls on the slit X when white light is admitted at E.

Let the slit Y correspond to another portion of the spectrum, say the green; then, if white light is admitted at Y, the prism, as seen by an eye at E, will be uniformly illuminated with green light; and if white light be admitted at X and Y simultaneously, the colour seen at E will be a compound of red and green, the proportions depending on the breadth of the slits and the intensity of the light which enters them. The third slit, Z, enables us to combine any three kinds of light in any given proportions, so that an eye at E shall see the face of the prism at P uniformly illuminated with the colour resulting from the combination of the three. The position of these three rays in the spectrum is found by admitting the light at E, and comparing the position of the slits with the position of the principal fixed lines; and the breadth of the slits is determined by means of the wedge.

At the same time white light is admitted through BC to the mirror of black glass at M, whence it is reflected to E, past the edge of the prism at P, so that the eye at E sees through the lens a field consisting of two portions, separated by the edge of the prism; that on the left hand being compounded of three colours of the spectrum refracted by the prism, while that on the right hand is white light reflected from the mirror. By adjusting the slits properly, these two portions of the field may be made equal, both in colour and brightness, so that the edge of the prism becomes almost invisible.

In making experiments, the instrument was placed on a table in a room moderately lighted, with the end AB turned towards a large board covered with white paper, and placed in the open air, so as to be uniformly illuminated by the sun. In this way the three slits and the mirror M were all illuminated with white light of the same intensity, and all were affected in the same ratio by any change of illumination; so that if the two halves of the field were rendered equal when the sun was under a cloud, they were found nearly correct when the sun again appeared. No experiments, however, were considered good unless the sun remained uniformly bright during the whole series of experiments.

After each set of experiments light was admitted at E, and the position of the fixed lines D and F of the spectrum was read off on the scale at AB. It was found that after

the instrument had been some time in use these positions were invariable, showing that the eye-hole, the prisms, and the scale might be considered as rigidly connected.

§ VI. *Method of determining the Wave-length corresponding to any point of the Spectrum on the Scale* AB.

Two plane surfaces of glass were kept apart by two parallel strips of goldbeaters' leaf, so as to enclose a stratum of air of nearly uniform thickness. Light reflected from this stratum of air was admitted at E, and the spectrum formed by it was examined at AB by means of a lens. This spectrum consists of a large number of bright bands, separated by dark spaces at nearly uniform intervals, these intervals, however, being considerably larger as we approach the violet end of the spectrum.

The reason of these alternations of brightness is easily explained. By the theory of NEWTON'S rings, the light reflected from a stratum of air consists of two parts, one of which has traversed a path longer than that of the other, by an interval depending on the thickness of the stratum and the angle of incidence. Whenever the interval of retardation is an exact multiple of a wave-length, these two portions of light destroy each other by interference; and when the interval is an odd number of half wave-lengths, the resultant light is a maximum.

In the ordinary case of NEWTON'S rings, these alternations depend upon the varying thickness of the stratum; while in this case a pencil of rays of different wave-lengths, but all experiencing the same retardation, is analysed into a spectrum, in which the rays are arranged in order of their respective wave-lengths. Every ray whose wave-length is an exact submultiple of the retardation will be destroyed by interference, and its place will appear dark in the spectrum; and there will be as many dark bands seen as there are rays whose wave-lengths fulfil this condition.

If, then, we observe the positions of the dark bands on the scale AB, the wave-lengths corresponding to these positions will be a series of submultiples of the retardation.

Let us call the first dark band visible on the red side of the spectrum zero, and let us number them in order 1, 2, 3, &c. towards the violet end. Let N be the number of undulations corresponding to the band zero which are contained in the retardation R; then if n be the number of any other band, $N+n$ will be the number of the corresponding wave-lengths in the retardation, or in symbols,

$$R=(N+n)\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.)$$

Now observe the position of two of FRAUNHOFER'S fixed lines with respect to the dark bands, and let n_1, n_2 be their positions expressed in the number of bands, whole or fractional, reckoning from zero. Let λ_1, λ_2 be the wave-lengths of these fixed lines as determined by FRAUNHOFER, then

$$R=(N+n_1)\lambda_1=(N+n_2)\lambda_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.)$$

whence

$$N=\frac{n_2\lambda_2-n_1\lambda_1}{\lambda_1-\lambda_2}=\frac{(n_2-n_1)}{\lambda_1-\lambda_2}\lambda_2-n_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.)$$

and
$$R=\frac{n_2-n_1}{\lambda_1-\lambda_2}\lambda_1\lambda_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.)$$

Having thus found N and R, we may find the wave-length corresponding to the dark band n from the formula
$$\lambda=\frac{R}{N+n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.)$$

In my experiments the line D corresponded with the seventh dark band, and F was between the 15th and 16th, so that $n_2=15{\cdot}7$. Here then for D,

$$\left.\begin{matrix} n_1=7 & \lambda_1=2175 \\ n_2=15{\cdot}7 & \lambda_2=1794 \end{matrix}\right\} \text{in Fraunhofer's measure,} \quad . \quad . \quad . \quad . \quad (11.)$$

and for F,

whence we find $N=34$, $R=89175$. . . . . (12.)

There were 22 bands visible, corresponding to 22 different positions on the scale AB, as determined 4th August, 1859.

Table I.

Band.	Scale.	Band.	Scale.	Band.	Scale.
$n=$ 1	17	$n=$ 9	36	$n=$ 16	57
2	19	10	39	17	61
3	21¼	11	42	18	65
4	23½	12	45	19	69
5	26	13	48	20	73
6	28½	14	51	21	77
7	31	15	54	22	82
8	33½				

Sixteen equidistant points on the scale were chosen for standard colours in the experiments to be described. The following Table gives the reading on the scale AB, the value of $N+n$, and the calculated wave-length for each of these:—

Table II.

Scale.	$(N+n)$.	Wave-length.	Colour.
20	36·4	2450	Red.
24	38·3	2328	Scarlet.
28	39·8	2240	Orange.
32	41·4	2154	Yellow.
36	42·9	2078	Yellow-green.
40	44·3	2013	Green.
44	45·7	1951	Green.
48	47·0	1879	Bluish green.
52	48·3	1846	Blue-green.
56	49·6	1797	Greenish blue.
60	50·8	1755	Blue.

TABLE II. (continued.)

Scale.	(N+n).	Wave-length.	Colour.
64	51·8	1721	Blue.
68	52·8	1688	Blue.
72	53·7	1660	Indigo.
76	54·7	1630	Indigo.
80	55·6	1604	Indigo.

Having thus selected sixteen distinct points of the spectrum on which to operate, and determined their wave-lengths and apparent colours, I proceeded to ascertain the mathematical relations between these colours in order to lay them down on NEWTON'S diagram. For this purpose I selected three of these as points of reference, namely, those at 24, 44, and 68 of the scale. I chose these points because they are well separated from each other on the scale, and because the colour of the spectrum at these points does not appear to the eye to vary very rapidly, either in hue or brightness, in passing from one point to another. Hence a small error of position will not make so serious an alteration of colour at these points, as if we had taken them at places of rapid variation; and we may regard the amount of the illumination produced by the light entering through the slits in these positions as sensibly proportional to the breadth of the slits.

(24) corresponds to a bright scarlet about one-third of the distance from C to D; (44) is a green very near the line E; and (68) is a blue about one-third of the distance from F to G.

§ VII. *Method of Observation.*

The instrument is turned with the end AB towards a board, covered with white paper, and illuminated by sunlight. The operator sits at the end AB, to move the sliders, and adjust the slits; and the observer sits at the end E, which is shaded from any bright light. The operator then places the slits so that their centres correspond to the three standard colours, and adjusts their breadths till the observer sees the prism illuminated with pure white light of the same intensity with that reflected by the mirror M. In order to do this, the observer must tell the operator what difference he observes in the two halves of the illuminated field, and the operator must alter the breadth of the slits accordingly, always keeping the centre of each slit at the proper point of the scale. The observer may call for more or less red, blue or green; and then the operator must increase or diminish the width of the slits X, Y, and Z respectively. If the variable field is darker or lighter than the constant field, the operator must widen or narrow all the slits in the same proportion. When the variable part of the field is nearly adjusted, it often happens that the constant white light from the mirror appears tinged with the complementary colour. This is an indication of what is required to make the resemblance of the two parts of the field of view perfect. When no difference can be detected between the two parts of the field, either in colour or in brightness, the observer must look away for some time, to relieve the strain on the eye, and then look again. If the eye thus refreshed still judges the two parts of the field to be equal, the observation

may be considered complete, and the operator must measure the breadth of each slit by means of the wedge, as before described, and write down the result as a colour-equation, thus—

Oct. 18, J. $18{\cdot}5(24)+27(44)+37(68)=W^{*}$. . . . . (13.)

This equation means that on the 18th of October the observer J. (myself) made an observation in which the breadth of the slit X was 18·5, as measured by the wedge, while its centre was at the division (24) of the scale; that the breadths of Y and Z were 27 and 37, and their positions (44) and (68); and that the illumination produced by these slits was exactly equal, in my estimation as an observer, to the constant white W.

The position of the slit X was then shifted from (24) to (28), and when the proper adjustments were made, I found a second colour-equation of this form—

Oct. 18, J. $16(28)+21(44)+37(68)=W$. . . . . (14.)

Subtracting one equation from the other and remembering that the figures in brackets are merely symbols of position, not of magnitude, we find

$$16(28)=18{\cdot}5(24)+6(44), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15.)$$

showing that (28) can be made up of (24) and (44), in the proportion of 18·5 to 6.

In this way, by combining each colour with two standard colours, we may produce a white equal to the constant white. The red and yellow colours from (20) to (32) must be combined with green and blue, the greens from (36) to (52) with red and blue, and the blues from (56) to (80) with red and green.

The following is a specimen of an actual series of observations made in this way by another observer (K.):—

TABLE III.

Oct. 13, 1859. Observer (K).

(X).	(Y).	(Z).	
$18\frac{1}{2}(24)$	$+32\frac{1}{2}(44)$	$+32\ (68)$	$=W^{*}$.
$17\frac{1}{2}(24)$	$+32\frac{1}{2}(44)$	$+63\ (80)$	$=W$.
$18\ (24)$	$+32\frac{1}{2}(44)$	$+35\ (72)$	$=W$.
$19\ (24)$	$+32\ (44)$	$+31\frac{1}{2}(68)$	$=W^{*}$.
$19\ (24)$	$+30\frac{1}{2}(44)$	$+35\ (64)$	$=W$.
$20\ (24)$	$+23\ (44)$	$+39\ (60)$	$=W$.
$21\ (24)$	$+14\ (44)$	$+58\ (56)$	$=W$.
$22\ (24)$	$+62\ (52)$	$+11\ (68)$	$=W$.
$22\ (24)$	$+42\ (48)$	$+29\frac{1}{2}(68)$	$=W$.
$19\ (24)$	$+31\frac{1}{2}(44)$	$+33\ (68)$	$=W^{*}$.
$16\ (24)$	$+28\ (40)$	$+32\frac{1}{2}(68)$	$=W$.
$6\ (24)$	$+27\ (36)$	$+32\frac{1}{2}(68)$	$=W$.
$23\ (32)$	$+11\frac{1}{2}(44)$	$+32\frac{1}{2}(68)$	$=W$.
$17\ (28)$	$+26\ (44)$	$+32\frac{1}{2}(68)$	$=W$.
$20\ (24)$	$+33\frac{1}{2}(44)$	$+32\frac{1}{2}(68)$	$=W^{*}$.
$46\ (20)$	$+33\ (44)$	$+30\ (68)$	$=W$.

The equations marked with an asterisk (*) are those which involve the three standard colours, and since every other equation must be compared with them, they must be often repeated.

The following Table contains the *means* of four sets of observations by the same observer (K):—

TABLE IV. (K.)

44·3(20)+31·0(44)+27·7(68)=W.
16·1(28)+25·6(44)+30·6(68)=W.
22·0(32)+12·1(44)+30·6(68)=W.
6·4(24)+25·2(36)+31·3(68)=W.
15·3(24)+26·0(40)+30·7(68)=W.
19·8(24)+35·0(46)+30·2(68)=W.
21·2(24)+41·4(48)+27·0(68)=W.
22·0(24)+62·0(52)+13·0(68)=W.
21·7(24)+10·4(44)+61·7(56)=W.
20·5(24)+23·7(44)+40·5(60)=W.
19·7(24)+30·3(44)+33·7(64)=W.
18·0(24)+31·2(44)+32·3(72)=W.
17·5(24)+30·7(44)+44·0(76)=W.
18·3(24)+33·2(44)+63·7(80)=W.

§ VIII. *Determination of the Average Error in Observations of different kinds.*

In order to estimate the degree of accuracy of these observations, I have taken the differences between the values of the three standard colours as originally observed, and their means as given by the above Table. The sum of all the errors of the red (24) from the means, was 31·1, and the number of observations was 42, which gives the average error ·74.

The sum of errors in green (44) was 48·0, and the number of observations 31, giving a mean error 1·55.

The sum of the errors in blue (68) was 46·9, and the number of observations 35, giving a mean error 1·16.

It appears therefore that in the observations generally, the average error does not exceed 1·5; and therefore the results, if confirmed by several observations, may safely be trusted to that degree of accuracy.

The equation between the three standard colours was repeatedly observed, in order to detect any alteration in the character of the light, or any other change of condition which would prevent the observations from being comparable with one another; and also because this equation is used in the reduction of all the others, and therefore requires

to be carefully observed. There are twenty observations of this equation, the mean of which gives

$$18{\cdot}6(24)+31{\cdot}4(44)+30{\cdot}5(68)=W^* \quad . \quad . \quad . \quad . \quad . \quad . \quad (16.)$$

as the standard equation.

We may use the twenty observations of this equation as a means of determining the relations between the errors in the different colours, and thus of estimating the accuracy of the observer in distinguishing colours.

The following Table gives the result of these operations, where R stands for (24), G for (44), and B for (68):—

TABLE V.—Mean Errors in the Standard Equation.

(R)= ·54	(G−B)=·99	(G+B)=2·31	$\sqrt{G^2+B^2}=1{\cdot}67$
(G)=1·22	(B−R)=·85	(B+R)=1·59	$\sqrt{B^2+R^2}=1{\cdot}26$
(B)=1·15	(R−G)=·86	(R+G)=1·57	$\sqrt{R^2+G^2}=1{\cdot}33$
(R+G+B)=2·67		$\sqrt{R^2+G^2+B^2}=1{\cdot}76$	

The first column gives the mean difference between the observed value of each of the colours and the mean of all the observations. The second column shows the average error of the observed *differences* between the values of the standards, from the mean value of those differences. The third column shows the average error of the *sums* of two standards, from the mean of such sums. The fourth column gives the square root of the sum of the squares of the quantities in the first column. I have also given the average error of the sum of R, G and B, from its mean value, and the value of $\sqrt{R^2+G^2+B^2}$.

It appears from the first column that the red is more accurately observed than the green and blue.

§ IX. *Relative Accuracy in Observations of Colour and of Brightness.*

If the errors in the different colours occurred perfectly independent of each other, then the probable mean error in the sum or difference of any two colours would be the square root of the sum of their squares, as given in the fourth column. It will be seen, however, that the number in the second column is always less, and that in the third always greater, than that in the fourth; showing that the errors are not independent of each other, but that positive errors in any colour coincide more often with positive than with negative errors in another colour. Now the *hue* of the resultant depends on the *ratios* of the components, while its *brightness* depends on their sum. Since, therefore, the difference of two colours is always more accurately observed than their sum, variations of *colour* are more easily detected than variations in *brightness*, and the eye appears to be a more accurate judge of the identity of colour of the two parts of the field than of their equal illumination. The same conclusion may be drawn from the value of the

mean error of the sum of the three standards, which is 2·67, while the square root of the sum of the squares of the errors is 1·76.

§ X. *Reduction of the Observations.*

By eliminating W from the equations of page 71 by means of the standard equation, we obtain equations involving each of the fourteen selected colours of the spectrum, along with the three standard colours; and by transposing the selected colour to one side of the equation, we obtain its value in terms of the three standards. If any of the terms of these equations are negative, the equation has no physical interpretation as it stands, but by transposing the negative term to the other side it becomes positive, and then the equation may be verified.

The following Table contains the values of the fourteen selected tints in terms of the standards. To avoid repetition, the symbols of the standard colours are placed at the head of each column.

TABLE VI.

Observer (K.).	(24.)	(44.)	(68.)
44·3(20)=	18·6	+ 0·4	+ 2·8
16·1(28)=	18·6	+ 5·8	− 0·1
22·0(32)=	18·6	+19·3	− 0·1
25·2(36)=	12·2	+31·4	− 0·8
26·0(40)=	3·3	+31·4	− 0·2
35·0(46)=−	1·2	+31·4	+ 0·3
41·4(48)=−	2·6	+31·4	+ 3·5
62·0(52)=−	3·4	+31·4	+17·5
61·7(56)=−	3·1	+21·0	+30·5
40·5(60)=−	1·9	+ 7·7	+30·5
33·7(64)=−	1·1	+ 1·1	+30·5
32·3(72)=+	0·6	+ 0·2	+30·5
44·0(76)=+	1·1	+ 0·7	+30·5
63·7(80)=+	0·3	− 1·8	+30·5

From these equations we may lay down a chart of the spectrum on NEWTON'S diagram by the following method:—Take any three points, A, B, C, and let A represent the standard colour (24), B (44), and C (68). Then, to find the position of any other colour, say (20), divide AC in P so that (18·6)AP=(2·8)PC, and then divide BP in Q so that (18·6+2·8)PQ=(0·4)QB. At the point Q the colour corresponding to (20) must be placed. In this way the diagram of fig. 4. Plate I. has been constructed from the observations of all the colours.

§ XI. *The Spectrum as laid down on* NEWTON'S *Diagram.*

The curve on which these points lie has this striking feature, that two portions of it are nearly, if not quite, straight lines. One of these portions extends from (24) to (46), and the other from (48) to (64). The colour (20), and those beyond (64), are not far from the line joining (24) and (68). The spectrum, therefore, as exhibited in NEWTON'S diagram, forms two sides of a triangle, with doubtful fragments of the third side. Now if three colours in NEWTON'S diagram lie in a straight line, the middle one is a compound of the two others. Hence all the colours of the spectrum may be compounded of those which lie at the angles of this triangle. These correspond to the following colours:—

TABLE VII.

	Scale.	Wave-length.	Index in water.	Wave-length in water.
R Scarlet . .	24	2328	1·332	1·747
G Green . . .	$46\frac{3}{4}$	1914	1·334	1·435
B Blue . . .	$64\frac{1}{2}$	1717	1·339	1·282

All the other colours of the spectrum may be produced by combinations of these; and since all natural colours are compounded of the colours of the spectrum, they may be compounded of these three primary colours. I have strong reason to believe that these are the three primary colours corresponding to three modes of sensation in the organ of vision, on which the whole system of colour, as seen by the normal eye, depends.

§ XII. *Results found by a second Observer.*

We may now consider the results of three series of observations made by myself (J.) as observer, in order to determine the relation of one observer to another in the perception of colour. The standard colours are connected by the following equation, as determined by six observations:—

$$18{\cdot}1(24)+27{\cdot}5(44)+37(68)=W^{*}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17.)$$

The average errors in these observations were—

TABLE VIII.

R, ·28	G+B, ·83	G−B, ·83	
G, ·83	B+R, ·42	B−R, ·28	R+G+B, ·95
B, ·16	R+G, ·95	R−G, ·72	

showing that in this case, also, the power of distinguishing *colour* is more to be depended on than that of distinguishing degrees of *illumination*.

The average error in the other observations from the means was ·64 for red, ·76 for green, and 1·02 for blue.

TABLE IX.

Observations by J., October 1859.

	(24.)	(44.)	(68.)
44·3(20)=	18·1	− 2·5	+ 2·3
16·0(28)=	18·1	+ 6·2	− 0·7
21·5(32)=	18·1	+25·2	− 0·7
19·3(36)=	8·1	+27·5	− 0·3
20·7(40)=	2·1	+27·5	− 0·5
52·3(48)=−	1·4	+27·5	+10·7
95·0(52)=−	2·4	+27·5	+37·0
51·7(56)=−	2·2	+ 4·8	+37·0
37·2(60)=−	1·2	+ 0·8	+37·0
36·7(64)=−	0·2	+ 0·8	+37·0
35·0(72)=+	0·6	− 0·2	+37·0
40·0(76)=+	0·9	+ 0·5	+37·0
51·0(80)=+	1·1	+ 0·5	+37·0

§ XIII. *Comparison of Results by* NEWTON'S *Diagram.*

The relations of the colours, as given by these observations, are laid down in fig. 5, Plate I. It appears from this diagram, that the positions of the colours lie nearly in a straight line from (24) to (44), and from (48) to (60). The colours beyond (60) are crowded together, as in the other diagram, and the observations are not yet sufficiently accurate to distinguish their relative positions accurately. The colour (20) at the red end of the spectrum is further from the line joining (24) and (68) than in the other diagram, but I have not obtained satisfactory observations of these extreme colours. It will be observed that (32), (36), and (40) are placed further to the right in fig. 5 than in fig. 4, showing that the second observer (J.) sees more green in these colours than the first (K.), also that (48), (52), (56), and (60) are much further up in fig. 5, showing that to the second observer they appear more blue and less green. These differences were well seen in making an observation. When the instrument was adjusted to suit the first observer (K.), then, if the selected colour were (32), (36), or (40), the second (J.), on looking into the instrument, saw it too green; but if (48), (52), (56), or (60) were the selected colour, then, if right to the first observer, it appeared too blue to the second. If the instrument were adjusted to suit the second observer, then, in the first case, the other saw red, and in the second green; showing that there was a real difference in the eyes of these two individuals, producing constant and measurable differences in the apparent colour of objects.

§ XIV. *Comparison by Curves of Intensity of the Primaries.*

Figs. 6 and 7, Plate I., are intended to indicate the intensities of the three standard

colours at different points of the spectrum. The curve marked (R) indicates the intensity of the red or (24), (G) that of green or (44), and (B) that of blue or (68). The curve marked (S) has its ordinates equal to the sum of the ordinates of the other three curves. The intensities are found by dividing every colour-equation by the coefficient of the colour on the left-hand side. Fig. 6 represents the results of observations by K, and fig. 7 represents those of J. It will be observed that the ordinates in fig. 7 are smaller between (48) and (56) than in fig. 6. This indicates the feeble intensity of certain kinds of light as seen by the eyes of J, which made it impossible to get observations of the colour (52) at all without making the slit so wide as to include all between (48) and (56).

This blindness of my eyes to the parts of the spectrum between the fixed lines E and F appears to be confined to the region surrounding the axis of vision, as the field of view, when adjusted for my eyes looking directly at the colour, is decidedly out of adjustment when I view it by indirect vision, turning the axis of my eye towards some other point. The prism then appears greener and brighter than the mirror, showing that the parts of my eye at a distance from the axis are more sensitive to this blue-green light than the parts close to the axis.

It is to be noticed that this insensibility is not to all light of a green or blue colour, but to light of a definite refrangibility. If I had a species of colour-blindness rendering me totally or partially insensible to that element of colour which most nearly corresponds with the light in question, then the light from the mirror, as well as that from the prism, would appear to me deficient in that colour, and I should still consider them chromatically identical; or if there were any difference, it would be the same for all colours nearly the same in appearance, such as those just beyond the line F, which appear to me quite bright.

We must also observe that the peculiarity is confined to a certain portion of the retina, which is known to be of a yellow colour, and which is the seat of several ocular phenomena observed by PURKINJE and WHEATSTONE, and of the sheaf or brushes seen by HAIDINGER in polarized light; and also that though, of the two observers whose results are given here, one is much more affected with this peculiarity than the other, both are less sensible to the light between E and F than to that on either side; and other observers, whose results are not here given, confirm this.

§ XV. *Explanation of the Differences between the two Observers.*

I think, therefore, that the yellow spot at the foramen centrale of SOEMMERING will be found to be the cause of this phenomenon, and that it absorbs the rays between E and F, and would, if placed in the path of the incident light, produce a corresponding dark band in the spectrum formed by a prism.

The reason why white light does not appear yellow in consequence, is that this absorbing action is constant, and we reckon as white the *mean* of all the colours we are accustomed to see. This may be proved by wearing spectacles of any strong colour for some

time, when we shall find that we judge white objects to be white, in spite of the rays which enter the eye being coloured.

Now ordinary white light is a mixture of all kinds of light, including that between E and F, which is partially absorbed. If, therefore, we compound an artificial white containing the absorbed ray as one of its three components, it will be much more altered by the absorption than the ordinary light, which contains many rays of nearly the same colour, which are not absorbed. On the other hand, if the artificial light do not contain the absorbed ray, it will be less altered than the ordinary light which contains it. Hence the greater the absorption the less green will those colours appear which are near the absorbed part, such as (48), (52), (56), and the more green will the colours appear which are not near it, such as (32), (36), (40). And these are the chief differences between fig. 4 and fig. 5.

I first observed this peculiarity of my eyes when observing the spectrum formed by a very long vertical slit. I saw an elongated dark spot running up and down in the blue, as if confined in a groove, and following the motion of the eye as it moved up or down the spectrum, but refusing to pass out of the blue into other colours. By increasing the breadth of the spectrum, the dark portion was found to correspond to the *foramen centrale*, and to be visible only when the eye is turned towards the blue-green between E and F. The spot may be well seen by first looking at a yellow paper, and then at a blue one, when the spot will be distinctly seen for a short time, but it soon disappears when the eye gets accustomed to the blue*.

I have been the more careful in stating this peculiarity of my eyes, as I have reason to believe that it affects most persons, especially those who can see HAIDINGER'S brushes easily. Such persons, in comparing their vision with that of others, may be led to think themselves affected with partial colour-blindness, whereas their colour-vision may be of the ordinary kind, but the rays which reach their sense of sight may be more or less altered in their proportions by passing through the media of the eye. The existence of real, though partial colour-blindness will make itself apparent, in a series of observations, by the discrepancy between the observed values and the means being greater in certain colours than in others.

§ XVI. *General Conclusions.*

Neither of the observers whose results are given here show any indications of colour-blindness, and when the differences arising from the absorption of the rays between E and F are put out of account, they agree in proving that there are three colours in the spectrum, red, green, and blue, by the mixtures of which colours chromatically identical with the other colours of the spectrum may be produced. The exact position of the red and blue is not yet ascertained; that of the green is $\frac{1}{4}$ from E towards F.

The orange and yellow of the spectrum are chromatically equivalent to mixtures of red and green. They are neither richer nor paler than the corresponding mixtures, and the only difference is that the mixture may be resolved by a prism, whereas the colour

* See the Report of the British Association for 1856, p. 12.

in the spectrum cannot be so resolved. This result seems to put an end to the pretension of yellow to be considered a primary element of colour.

In the same way the colours from the primary green to blue are chromatically identical with mixtures of these; and the extreme ends of the spectrum are probably equivalent to mixtures of red and blue, but they are so feeble in illumination that experiments on the same plan with the rest can give no result, but they must be examined by some special method. When observations have been obtained from a greater number of individuals, including those whose vision is dichromatic, the chart of the spectrum may be laid down independently of accidental differences, and a more complete discussion of the laws of the sensation of colour attempted.

POSTSCRIPT.

Received May 8,—Read May 24, 1860.

Since sending the above paper to the Royal Society, I have obtained some observations of the colour of the spectrum by persons whose vision is "dichromic," and who are therefore said to be "colour-blind."

The instrument used in making these observations was similar in principle to that formerly described, except that, in order to render it portable, the rays are reflected back through the prisms, nearly in their original direction; thus rendering one of the limbs of the instrument unnecessary, and allowing the other to be shortened considerably on account of the greater angular dispersion. The principle of reflecting light, so as to pass twice through the same prism, was employed by me in an instrument for combining colours made in 1856, and a reflecting instrument for observing the spectrum has been constructed independently by M. Porro.

Light from a sheet of paper illuminated by sunlight is admitted at the slits X, Y, Z (fig. 8, Plate II.), falls on the prisms P and P′ (angles=45°), then on a concave silvered glass, S, radius 34 inches. The light, after reflexion, passes again through the prisms P′ and P, and is reflected by a small mirror, e, to the slit E, where the eye is placed to receive the light compounded of the colours corresponding to the positions and breadths of the slits X, Y, and Z.

At the same time, another portion of the light from the illuminated paper enters the instrument at BC, is reflected at the mirror M, passes through the lens L, is reflected at the mirror M′, passes close to the edge of the prism P, and is reflected along with the coloured light at e, to the eye-slit at E.

In this way the compound colour is compared with a constant white light in optical juxtaposition with it. The mirror M is made of silvered glass, that at M′ is made of glass roughened and blackened at the back, to reduce the intensity of the constant light to a convenient value for the experiments.

This instrument gives a spectrum in which the lines are very distinct, and the length of the spectrum from A to H is 3·6 inches. The outside measure of the box is 3 feet 6 inches, by 11 inches by 4 inches, and it can be carried about, and set up in any position, without readjustment. It was made by Messrs. SMITH and RAMAGE of Aberdeen.

In obtaining observations from colour-blind persons, two slits only are required to produce a mixture chromatically equivalent to white; and at one point of the spectrum the colour of the pure rays appears identical with white. This point is near the line F, a little on the less refrangible side. From this point to the more refrangible end of the spectrum appears to them "blue." The colours on the less refrangible side appear to them all of the same quality, but of different degrees of brightness; and when any of them are made sufficiently bright, they are called "yellow." It is convenient to use the term "yellow" in speaking of the colours from red to green inclusive, since it will be found that a dichromic person in speaking of red, green, orange, and brown, refers to different degrees of brightness or purity of a single colour, and not to different colours perceived by him. This colour we may agree to call "yellow," though it is not probable that the sensation of it is like that of yellow as perceived by us.

Of the three standard colours which I formerly assumed, the red appears to them "yellow," but so feeble that there is not enough in the whole red division of the spectrum to form an equivalent to make up the standard white. The green at E appears a good "yellow," and the blue at $\frac{3}{4}$ from F towards G appears a good "blue." I have therefore taken these as standard colours for reducing dichromic observations. The three standard colours will be referred to as (104), (88), and (68), these being the positions of the red, green, and blue on the scale of the new instrument.

Mr. JAMES SIMPSON, formerly student of Natural Philosophy in my class, has furnished me with thirty-three observations taken in good sunlight. Ten of these were between the two standard colours, and give the following result:—

$$33{\cdot}7(88)+33{\cdot}1(68)=W. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

The mean errors of these observations were as follows:—

Error of (88)=2·5; of (68)=2·3; of (88)+(68)=4·8; of (88)−(68)=1·3.

The fact that the mean error of the sum was so much greater than the mean error of the difference, indicates that in this case, as in all others that I have examined, observations of equality of tint can be depended on much more than observations of equality of illumination or brightness.

From six observations of my own, made at the same time, I have deduced the "trichromic" equation

$$22{\cdot}6(104)+26(88)+37{\cdot}4(68)=W. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

If we suppose that the light which reached the organ of vision was the same in both cases, we may combine these equations by subtraction, and so find

$$22{\cdot}6(104)-7{\cdot}7(88)+4{\cdot}3(68)=D, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

where D is that colour, the absence of the sensation of which constitutes the defect of the dichromic eye. The sensation which I have in addition to those of the dichromic eye is therefore similar to the full red (104), but different from it, in that the red (104) has 7·7 of green (88) in it which must be removed, and 4·3 of blue (68) substituted. This agrees pretty well with the colour which Mr. POLE* describes as neutral to him, though crimson to others. It must be remembered, however, that different persons of ordinary vision require different proportions of the standard colours, probably owing to differences in the absorptive powers of the media of the eye, and that the above equation (2.), if observed by K, would have been

$$23(104)+32(88)+31(68)=W; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

and the value of D, as deduced from these observers, would have been

$$23(104)-1{\cdot}7(88)-1{\cdot}1(68)=D, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

in which the defective sensation is much nearer to the red of the spectrum. It is probably a colour to which the extreme red of the spectrum tends, and which differs from the extreme red only in not containing that small proportion of "yellow" light which renders it visible to the colour-blind.

From other observations by Mr. SIMPSON the following results have been deduced:—

TABLE *a*.

	(88).	(68).		(88).	(68).
(99·2+)=	33·7	1·9			
31·3(96)=	33·7	2·1	100(96)=	108	7
28 (92)=	33·7	1·4	100(92)=	120	5
33·7(88)=	33·7	0	100(88)=	100	0
54·7(84)=	33·7	6·1	100(84)=	61	11
71 (82)=	33·7	15·1	100(82)=	47	21
99 (80)=	33·7	33·1	100(80)=	34	33
70 (78)=	15·7	33·1	100(78)=	22	47
56 (76)=	5·7	33·1	100(76)=	10	59
36 (72)=−	0·3	33·1	100(72)=−	1	92
33·1(68)=	0	33·1	100(68)=	0	100
40 (64)=	0·2	33·1	100(64)=	0	83
55·5(60)=	1·7	33·1	100(60)=	3	60
(57−) =−	0·3	33·1			

In the Table on the left side (99·2+) means the whole of the spectrum beyond (99·2) on the scale, and (57−) means the whole beyond (57) on the scale. The position of the fixed lines with reference to the scale was as follows:—

A, 116; *a*, 112; B, 110; C, 106; D, 98·3; E, 88; F, 79; G, 61; H, 44.

The values of the standard colours in different parts of the spectrum are given on the

* Philosophical Transactions, 1859, Part I. p. 329.

right side of the above Table, and are represented by the curves of fig. 9, Plate II., where the left-hand curve represents the intensity of the "yellow" element, and the right-hand curve that of the "blue" element of colour as it appears to the colour-blind.

The appearance of the spectrum to the colour-blind is as follows:—

From A to E the colour is pure "yellow" very faint up to D, and reaching a maximum between D and E. From E to one-third beyond F towards G the colour is mixed, varying from "yellow" to "blue," and becoming neutral or "white" at a point near F. In this part of the spectrum, the total intensity, as given by the dotted line, is decidedly less than on either side of it, and near the line F, the retina close to the "yellow spot" is less sensible to light than the parts further from the axis of the eye. This peculiarity of the light near F is even more marked in the colour-blind than in the ordinary eye. Beyond F the "blue" element comes to a maximum between F and G, and then diminishes towards H; the spectrum from this maximum to the end being pure "blue."

In fig. 10, Plate II. these results are represented in a different manner. The point D, corresponding to the sensation wanting in the colour-blind, is taken as the origin of coordinates, the "yellow" element of colour is represented by distances measured horizontally to the right from D, and the "blue" element by distances measured vertically from the horizontal line through D. The numerals indicate the different colours of the spectrum according to the scale shown in fig. 9, and the coordinates of each point indicate the composition of the corresponding colour. The triangle of colours is reduced, in the case of dichromic vision, to a straight line "B" "Y," and the proportions of "blue" and "yellow" in each colour are indicated by the ratios in which this line is cut by the line from D passing through the position of that colour.

The results given above were all obtained with the light of white paper, placed in clear sunshine. I have obtained similar results, when the sun was hidden, by using the light of uniformly illuminated clouds, but I do not consider these observations sufficiently free from disturbing circumstances to be employed in calculation. It is easy, however, by means of such observations, to verify the most remarkable phenomena of colour-blindness, as for instance, that the colours from red to green appear to differ only in brightness, and that the brightness may be made identical by changing the width of the slit; that the colour near F is a neutral tint, and that the eye in viewing it sees a dark spot in the direction of the axis of vision; that the colours beyond are all blue of different intensities, and that any "blue" may be combined with any "yellow" in such proportions as to form "white." These results I have verified by the observations of another colour-blind gentleman, who did not obtain sunlight for his observations; and as I have now the means of carrying the requisite apparatus easily, I hope to meet with other colour-blind observers, and to obtain their observations under more favourable circumstances.

On the Comparison of Colour-blind with ordinary Vision by means of Observations with Coloured Papers.

In March 1859 I obtained a set of observations by Mr. SIMPSON, of the relations

between six coloured papers as seen by him. The experiments were made with the colour-top in the manner described in my paper in the Transactions of the Royal Society of Edinburgh, vol. xxi. pt. 2. p. 286; and the colour-equations were arranged so as to be equated to zero, as in those given in the Philosophical Magazine, July 1857. The colours were,—Vermilion (V), ultramarine (U), emerald-green (G), ivory-black (B), snow-white (W), and pale chrome-yellow (Y). These six colours afford fifteen colour-blind equations, since four colours enter into each equation. Fourteen of these were observed by Mr. SIMPSON, and from these I deduced three equations, giving the relation of the three standards (V), (U), (G) to the other colours, according to his kind of vision. From these three equations I then deduced fifteen equations, admitting of comparison with the observed equations, and necessarily consistent in themselves.

The comparison of these equations furnishes a test of the truth of the theory that the colour-blind see by means of two colour-sensations, and that therefore every colour may be expressed in terms of *two* given colours, just as in ordinary vision it may be expressed in terms of three given colours. The one set of equations are each the result of a single observation; the other set are deduced from three equations in accordance with this theory, and the two sets agree to within an average error $=2{\cdot}1$.

TABLE *b*.

	V.	U.	G.	B.	W.	Y.	
1. Observed . . .	0	0	−100	+45	+22	+33	=0.
Calculated . .	0	0	−100	+37·5	+26·5	+36	=0.
2. Observed . . .	0	+58	0	−69	−31	+42	=0.
Calculated . . .	0	+58·3	0	−67·3	−32·7	+41·7	=0.
3. Observed . . .	0	+32	−100	0	+12	+56	=0.
Calculated . .	0	+32·3	−100	0	+ 8·3	+59·4	=0.
4. Observed . . .	0	+38	− 89	−11	0	+62	=0.
Calculated . .	0	+40	− 85	−15	0	+60	=0.
5. Observed . . .	0	+32	+ 68	−60	−40	0	=0.
Calculated . .	0	+34	+ 66	−63·5	−36·5	0	=0.
6. Observed . . .	−100	0	0	+82	+ 5	+13	=0.
Calculated . .	−100	0	0	+83·9	+ 4·5	+11·6	=0.
7. Observed . . .	+ 47	0	−100	0	+22	+31	=0.
Calculated . .	+ 44·7	0	−100	0	+24·5	+30·8	=0.
8. Observed . . .	−100	0	+ 20	+77	0	+ 3	=0.
Calculated . .	−100	0	+ 17	+77·5	0	+ 5·5	=0.
9. Not observed.							
Calculated . .	+ 96	0	− 31	−69	+ 4	0	=0.

TABLE δ (continued).

	V.	U.	G.	B.	W.	Y.	
10. Observed . . .	− 70	+53	0	0	−30	+47	=0.
Calculated . .	− 73·5	+53	0	0	−26·5	+47	=0.
11. Observed . . .	−100	+ 8	0	+71	0	+21	=0.
Calculated . .	−100	+ 8	0	+74·5	0	+17·5	=0.
12. Observed . . .	+ 85	+15	0	−88	−12	0	=0.
Calculated . .	+ 86	+14	0	−88·5	−11·5	0	=0.
13. Observed . . .	− 20	+39	− 80	0	0	+61	=0.
Calculated . .	− 19	+40	− 81	0	0	+60	=0.
14. Observed . . .	− 66	+30	+ 70	0	−34	0	=0.
Calculated . .	− 70	+27	+ 73	0	−30	0	=0.
15. Observed . . .	+100	− 2	− 27	−71	0	0	=0.
Calculated . .	+ 96	+ 4	− 24	−76	0	0	=0.

But, according to our theory, colour-blind vision is not only dichromic, but the two elements of colour are identical with two of the three elements of colour as seen by the ordinary eye; so that it differs from ordinary vision only in not perceiving a particular colour, the relation of which to known colours may be numerically defined. This colour may be expressed under the form

$$aV+\delta U+cG=D, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16.)$$

where V, U, and G are the standard colours used in the experiments, and D is the colour which is visible to the ordinary eye, but invisible to the colour-blind. If we know the value of D, we may always change an ordinary colour-equation into a colour-blind equation by subtracting from it nD (n being chosen so that one of the standard colours is eliminated), and adding n of black.

In September 1856 I deduced, from thirty-six observations of my own, the chromatic relations of the same set of six coloured papers. These observations, with a comparison of them with the trichromic theory of vision, are to be found in the 'Philosophical Magazine' for July 1857. The relations of the six colours may be deduced from two equations, of which the most convenient form is

V.	U.	G.	B.	W.	Y.	
+39·7	+26·6	+33·7	−22·7	−77·3	0	=0. . . . (17.)
−62·4	+18·6	−37·6	0	+45·7	+35·7	=0. . . . (18.)

The value of D, as deduced from a comparison of these equations with the colour-blind equations, is

$$1{\cdot}198V+0{\cdot}078U-0{\cdot}276G=D. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19.)$$

By making D the same thing as black (B), and eliminating W and Y respectively from the two ordinary colour-equations by means of D, we obtain three colour-blind equa-

tions, calculated from the ordinary equations and consistent with them, supposing that the colour (D) is black to the colour-blind.

The following Table is a comparison of the colour-blind equations deduced from Mr. SIMPSON's observations alone, with those deduced from my observations and the value of D.

TABLE *c*.

	V.	U.	G.	B.	W.	Y.
(15) Calculated . .	+96	+ 4	−24	−76	0	0
By (19)	+93·9	+ 6·1	−21·7	−78·3	0	0
(14) Calculated . .	−70	+27	+73	0	−30	0
By (17) and (19) . .	−70	+27·2	−72·8	0	−30	0
(13) Calculated . .	−19	+40	−81	0	0	+60
By (18) and (19) . .	−13·6	+38·5	−86·4	0	0	+61·5

The average error here is 1·9, smaller than the average error of the individual colour-blind observations, showing that the theory of colour-blindness being the want of a certain colour-sensation which is one of the three ordinary colour-sensations, agrees with observation to within the limits of error.

In fig. 11, Plate II. I have laid down the chromatic relations of these colours according to NEWTON's method. V (vermilion), U (ultramarine), and G (emerald-green) are assumed as standard colours, and placed at the angles of an equilateral triangle. The position of W (white) and Y (pale chrome-yellow) with respect to these are laid down from equations (17.) and (18.), deduced from my own observations. The positions of the defective colour, of white, and of yellow, as deduced from Mr. SIMPSON's equations alone, are given at "*d*," "*w*," and "*y*." The positions of these points, as deduced from a combination of these equations with my own, are given at "D," "W," and "Y." The difference of these positions from those of "*d*," "*w*," and "*y*," shows the amount of discrepancy between observation and theory.

It will be observed that D is situated near V (vermilion), but that a line from D to W cuts UV at C near to V. D is therefore a red colour, not scarlet, but further from yellow. It may be called crimson, and may be *imitated* by a mixture of 86 vermilion and 14 ultramarine. This compound colour will be of the same *hue* as D; but since C lies between D and W, C must be regarded as D diluted with a certain amount of white; and therefore D must be imagined to be like C in hue, but without the intermixture of white which is unavoidable in actual pigments, and which reduces the purity of the tint.

Lines drawn from D through "W" and "Y," the colour-blind positions of white and yellow, pass through W and Y, their positions in ordinary vision. The reason why they do not coincide with W and Y, is that the white and yellow papers are much brighter than the colours corresponding to the points W and Y of the triangle V, U, G; and therefore lines from D, which represent them in intensity as well as in quality, must be longer than DW and DY in the proportion of their brightness.

V. *On the Effect of the presence of Metals and Metalloids upon the Electric Conducting Power of Pure Copper.* By A. MATTHIESSEN, *Ph.D.*, *and* M. HOLZMANN, *Ph.D.* *Communicated by Professor* WHEATSTONE, *F.R.S.*

Received March 14,—Read April 26, 1860.

As the electric conducting power of copper varies so much according to different experimenters, we thought it would be of some interest to study the causes of these differences; and on comparing the values found for copper, we find that, taking silver =100, copper conducts according to

BECQUEREL*	RIESS†	LENZ‡	DAVY§	CHRISTIE§	HARRIS§	BUFF‖	POUILLET¶	ARNDTSEN**
95·3	67·2	73·4	91·2	66·0	100·0	95·4	73·0	98·7

The temperatures at which the above observations were made are only given in the cases of BECQUEREL, LENZ and ARNDTSEN, who compared copper at 0° C. with silver at 0° C. =100.

We prepared therefore pure copper,—

1. By precipitating with sulphuretted hydrogen the purest commercial sulphate of copper dissolved in water acidulated with sulphuric acid, dissolving the washed sulphide in nitric acid, precipitating at a boiling temperature by carbonate of soda in excess, and finally reducing the oxide of copper with pure hydrogen.

2. By precipitating sulphate of copper galvanoplastically by a very weak current.

We have also tested the galvanoplastic copper of commerce, and have found that its conducting power is the same as that of the copper we prepared.

The method used for the determinations was the same as that described in the Philosophical Magazine (February 1857). The diameters of the wires used were about 0·25 to 0·5 millim., and the lengths from 0·5 to 1·5 metre; and of each specimen of copper or alloy two or three determinations were made with wires of different diameters.

The following are the results obtained with pure copper, compared with a hard drawn silver wire =100 at 0° C. (all the wires were hard drawn):—

		Means.
I. Copper purified by the above method (1) . . .	*a*. 92·63 at 18°·0 *b*. 93·36 at 19°·2	93·00 at 18°·6
II. Copper, galvanoplastic, not fused	*a*. 93·81 at 19°·7 *b*. 93·56 at 20°·5 *c*. 93·00 at 20°·4	93·46 at 20°·2

* Ann. de Chim. et de Phys. Sér. 3. vol. xvii. p. 242.
† POGGENDORFF's Annalen, vol. xlv. p. 20.
‡ Ibid. p. 105.
§ GMELIN, vol. i. p. 289.
‖ BUFF, Gründriss der Physik, 348.
¶ MÜLLER, Lehrbuch der Physik, p. 202.
** POGGENDORFF's Annalen, vol. cv. p. 1.

		Means.
III. Copper, galvanoplastic commercial, not fused	*a.* 92·24 at 18°·0 *b.* 93·01 at 18·5 *c.* 93·81 at 18·7	93·02 at 18°·4
IV. Copper No. 3, fused in a porcelain tube in hydrogen	*a.* 92·22 at 19·3 *b.* 93·30 at 19·3	92·76 at 19·3
V. Copper No. 3, fused, as will be presently described	*a.* 92·57 at 17·8 *b.* 93·40 at 17·2	92·99 at 17·5

The mean of the above twelve determinations gives 93·08 at 18°·9 for the conducting power of pure copper.

Peltier* and others have already observed that annealed copper wire conducts better than hard drawn wire; and on repeating the experiments with hard drawn wires from copper No. 2, and which were annealed in a current of pure hydrogen, we found the following numbers:—

I.	Hard drawn	95·31 at 11°·0
	Annealed	97·83 at 11·0
II.	Hard drawn	95·72 at 11·0
	Annealed	98·02 at 11·0

which makes a difference in the conducting powers of hard drawn and annealed wires of about 2·5 per cent.; much greater, however, is the difference between hard drawn and annealed silver wires, as the following experiments show:—

I.	*a.* Hard drawn . . .	95·28 at 14°·6
	b. Annealed	103·98 at 14·8
II.	*a.* Hard drawn . . .	95·36 at 14·6
	b. Annealed	103·33 at 14·6

We will now proceed to describe what is the effect of the metalloids, and afterwards of the metals, on the conducting power of copper.

1. *Effect of Oxygen* (*Suboxide of Copper*).

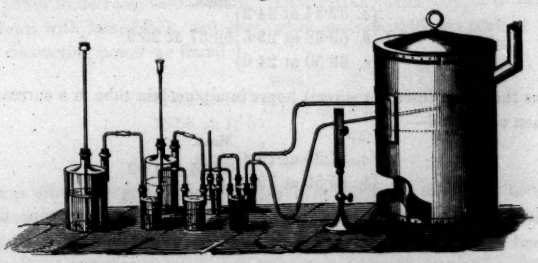
Copper readily absorbs oxygen from the air when in a fused state; and it is supposed to be present as suboxide, which it retains very obstinately; and in fact we may lead hydrogen over fused copper, in a porcelain tube, for hours without completely reducing the suboxide. It is also very difficult to prevent the oxygen being absorbed during casting, &c. In order to prevent all these sources of error, we thought that in making the alloys of copper by the following method, we might obviate them:—

Fig. 1 shows the disposition of the apparatus. In the furnace-door communicating with a closed muffle are two holes; through the upper one passes a glass tube connected

* Ann. de Chim. et de Phys. lvi. p. 371.

with a carbonic acid gas apparatus, through the lower one passes a clay tobacco-pipe, to the stem of which is joined the bottle evolving hydrogen. The hydrogen is washed with

Fig. 1.



potash, nitrate of silver, and concentrated sulphuric acid, and the carbonic acid gas with bicarbonate of potash and strong sulphuric acid. The metal (about 8 grms. were taken for each experiment) was placed in the bowl of the pipe, and so fused in a current of hydrogen; when fused, the hydrogen bubbled up through the melted metal; thus by offering a fresh surface to the hydrogen, any suboxide that might be present was reduced; and when making the copper alloys complete mixture was effected. When the hydrogen had passed through for a certain length of time, the india-rubber tubing was disconnected from the sulphuric acid bottle, and the fused metal carefully sucked into the pipe-stem, forming, as shown by fig. 2, a wire which might, if necessary, be drawn finer. The carbonic acid gas was used to help to drive the air out of the muffle, as well as in some experiments which will be presently detailed.

Fig. 2.

In order to test the method, copper No. 3 was fused in the pipe, and kept so for about half an hour, when we found the conducting power—

		Mean.
a. 92·57 at 17°·8	}	92·99 at 17°·5.
b. 93·40 at 17·2		

In this manner we have been able to reduce the suboxide in the copper by degrees: all the alloys made were fused in this manner, only substituting carbonic acid gas in cases in which hydrogen could not be employed.

We did not try to determine quantitatively the amount of suboxide present in the copper, as we know of no method which will give results which can be depended upon*. We shall only give the conducting power of copper that had been fused in contact with

* Dick (Phil. Mag. June 1858) could not obtain any good results by any of the known methods. All the experiments which we have made agree with his, especially concerning the action of ammonia on copper.

air. Thus copper, chemically purified, was fused with borax and chloride of sodium (the flux not quite covering the surface of the melted copper). The conducting power of this specimen was

$$\text{I.}\begin{cases} a.\ 69{\cdot}44 \text{ at } 24{\cdot}2^\circ \\ b.\ 69{\cdot}38 \text{ at } 23{\cdot}5 \\ c.\ 69{\cdot}30 \text{ at } 24{\cdot}0 \end{cases}\Big\}\text{Mean. } 69{\cdot}37 \text{ at } 23{\cdot}9^\circ$$

This was then kept fused for several hours in a porcelain tube in a current of hydrogen; it then conducted—

$$\text{II.}\begin{cases} a.\ 87{\cdot}20 \text{ at } 18{\cdot}8^\circ \\ b.\ 85{\cdot}50 \text{ at } 19{\cdot}0 \end{cases}\Big\}\text{Mean. } 86{\cdot}35 \text{ at } 18{\cdot}9^\circ$$

This was next treated in the above-described manner in the tobacco-pipe, first for half an hour, and then for three hours, which caused the conducting powers to increase to the following values:—

$$\text{III. After half an hour}\begin{cases} a.\ 89{\cdot}32 \text{ at } 17{\cdot}0^\circ \\ b.\ 91{\cdot}07 \text{ at } 17{\cdot}8 \\ c.\ 88{\cdot}40 \text{ at } 17{\cdot}4 \end{cases}\Big\}\text{Means. } 89{\cdot}57 \text{ at } 17{\cdot}4^\circ$$

$$\text{IV. After three hours}\begin{cases} a.\ 92{\cdot}63 \text{ at } 18{\cdot}0 \\ b.\ 93{\cdot}36 \text{ at } 19{\cdot}2 \end{cases}\Big\} 93{\cdot}00 \text{ at } 18{\cdot}6$$

Similar results were obtained with galvanoplastically precipitated copper, which had been fused in contact with air under a small quantity of borax and chloride of sodium.

$$\text{I. Fused in contact with air}\begin{cases} a.\ 73{\cdot}20 \text{ at } 19{\cdot}3^\circ \\ b.\ 73{\cdot}08 \text{ at } 19{\cdot}4 \\ c.\ 73{\cdot}69 \text{ at } 19{\cdot}8 \end{cases}\Big\}\text{Means. } 73{\cdot}32 \text{ at } 19{\cdot}5^\circ$$

$$\text{II. No. 1, fused in a tobacco-pipe for half an hour, as above described}\begin{cases} a.\ 76{\cdot}27 \text{ at } 17{\cdot}6 \\ b.\ 75{\cdot}55 \text{ at } 17{\cdot}7 \\ c.\ 75{\cdot}38 \text{ at } 17{\cdot}8 \end{cases}\Big\} 75{\cdot}73 \text{ at } 17{\cdot}7$$

$$\text{III. No. 1, fused one hour in pipe}\begin{cases} a.\ 83{\cdot}14 \text{ at } 16{\cdot}8 \\ b.\ 82{\cdot}25 \text{ at } 17{\cdot}0 \end{cases}\Big\} 82{\cdot}70 \text{ at } 16{\cdot}9$$

$$\text{IV. No. 1, fused for one hour and three-quarters in pipe}\begin{cases} a.\ 90{\cdot}36 \text{ at } 19{\cdot}7 \\ b.\ 91{\cdot}00 \text{ at } 19{\cdot}7 \end{cases}\Big\} 90{\cdot}68 \text{ at } 19{\cdot}7$$

$$\text{V. No. 1, fused for three hours in pipe}\begin{cases} a.\ 91{\cdot}92 \text{ at } 18{\cdot}5 \\ b.\ 92{\cdot}76 \text{ at } 18{\cdot}1 \end{cases}\Big\} 92{\cdot}34 \text{ at } 18{\cdot}3$$

From the above experiments we see how difficult it is to reduce the whole of the suboxide; a fact, which explains the reason why no good determinations as to the amount of oxygen present in copper have as yet been obtained.

2. *Effect of Carbon.*

According to KARSTEN*, copper takes up 0·2 per cent. of carbon; we could not, however, obtain wires containing more than 0·05 per cent. This small quantity causes the conducting power to decrease considerably. Thus galvanoplastic copper in small pieces was fused down with lamp-black, and gave, upon analysis, 0·05 per cent. of carbon†; and for the conducting power we found

	Mean.
74·29 at 18°·1 75·53 at 18°·5	74·91 at 18°·3

3. *Effect of Phosphorus.*

Phosphorus alters the properties of copper to a very great extent; it becomes very much harder, and its tenacity is greatly impaired. Of all the impurities, this has the greatest reducing effect on the conducting power of copper.

Red phosphorus was thrown on melted copper in a tobacco-pipe and re-fused. The amount of phosphorus was determined as phosphate of magnesia.

		Means.
I. Copper with 2·5 per cent. of phosphorus	*a.* 7·37 at 17°·0 *b.* 7·11 at 18·0	7·24 at 17°·5
II. Copper with 0·95 per cent. of phosphorus	*a.* 23·43 at 22·3 *b.* 23·05 at 22·0	23·24 at 22·1
III. Copper with 0·13 per cent. of phosphorus	*a.* 67·88 at 20·0 *b.* 67·46 at 20·0	67·67 at 20·0

4. *Effect of Sulphur, Selenium, and Tellurium.*

Sulphide of copper does not appear to dissolve in copper, but merely to mix with it mechanically. It makes the copper very brittle; and although we succeeded in drawing a wire which contained, according to the analysis, 0·18 per cent. of sulphur, the values obtained for the conducting power did not agree at all with each other. The mean of four determinations gave 88·58 at 19°·4.

Traces of selenium and tellurium make copper so rotten that we were unable to draw it.

5. *Effect of Arsenic.*

When arsenic is thrown upon melted copper the greater part of it is absorbed, whilst a part volatilizes; and on re-fusing the alloy formed, if a large quantity of arsenic has been used, it has a dingy grey colour, and is very hard and brittle. We managed to draw an alloy containing 5·40 per cent. of arsenic to the diameter of 0·29 millim.; and

* SCHWEIGGER's Journal für Chemie u. Physik, lxvi. p. 395.

† We repeated this experiment several times, but could not again make the alloy. In all probability, therefore, the carbon found was only mechanically mixed with copper.

had we had draw-plates with finer holes at our disposal, we might have drawn it much finer,—a fact, which does not at all agree with the assertions lately made, that copper with a small amount of arsenic cannot be drawn into fine wire. The arsenic was determined as arseniate of magnesia. The following values show that arsenic greatly reduces the conducting power of copper:—

		Means.
I. Copper with 5·40 per cent. of arsenic	*a.* 6·17 at 16°·7 *b.* 6·19 at 17°·0	6·18 at 16°·8
II. Copper with 2·80 per cent. of arsenic	*a.* 12·97 at 18°·8 *b.* 13·38 at 19°·4	13·14 at 19°·1
III. Copper with traces of arsenic	*a.* 57·72 at 19°·5 *b.* 57·89 at 19°·9	57·80 at 19°·7

6. *Effect of Heating in a current of Ammonia.*

Several experimenters state, that when copper is heated in ammonia, the gas is decomposed and nitride of copper formed, a fact which Schrötter* disputes, and has been proved totally incorrect by Dick. We repeated the experiment by heating a copper wire, whose conducting power had been previously determined, for a quarter of an hour in a current of dry ammonia; when cold, the conducting power was found the same, and the wire was as ductile as before. In all probability the reason why in the experiments of previous observers the copper became brittle, was (as already suggested by Dick) that they used copper containing suboxide.

7. *Effect of the Metals.*

The electric conductivity of copper is not so much impaired by the presence of small quantities of foreign metals as by that of the metalloids; it is, however, very considerably diminished by iron and tin.

The union of the copper with the other metals was effected in the manner before described, which offers in this case the additional advantage, that, by the constant movement caused by the hydrogen in the melted metals, the most intimate combination results. The amount of the metals thus alloyed with the copper was determined by analysis.

		Means.
I. Copper† alloyed with 3·20 per cent. of zinc‡	*a.* 56·96 at 10°·0 *b.* 57·01 at 10°·6	56·98 at 10°·3
II. Copper with 1·60 per cent. of zinc	*a.* 76·25 at 15°·2 *b.* 76·45 at 16°·4	76·35 at 15°·8
III. Copper with traces of zinc	*a.* 85·67 at 18°·0 *b.* 84·43 at 20°·0	85·05 at 19°·0

* Gmelin, vol. iii. p. 416.

† All wires hard drawn.

‡ All the metals employed were pure.

		Means.
IV. Copper with 1·06 per cent. of iron	*a.* 27·44 at 14°·2 *b.* 26·46 at 12°·0	26·95 at 13°·1
V. Copper with 0·48 per cent. of iron	*a.* 34·40 at 11°·0 *b.* 34·72 at 11°·4	34·56 at 11°·2
VI. Copper with 4·90 per cent. of tin	*a.* 19·35 at 14°·2 *b.* 19·60 at 14°·6	19·47 at 14°·4
VII. Copper with 2·52 per cent. of tin	*a.* 32·49 at 17°·0 *b.* 32·79 at 17°·2	32·64 at 17°·1
VIII. Copper with 1·33 per cent. of tin	*a.* 48·76 at 16°·8 *b.* 48·28 at 16°·8	48·52 at 16°·8
IX. Copper with 2·45 per cent. of silver	*a.* 80·01 at 19°·6 *b.* 79·21 at 19°·8 *c.* 78·93 at 19°·8	79·38 at 19°·7
X. Copper with 1·22 per cent. of silver	*a.* 87·61 at 20°·6 *b.* 86·65 at 20°·6 *c.* 86·46 at 21°·0	86·91 at 20°·7
XI. Copper with 3·50 per cent. of gold	*a.* 65·10 at 18°·0 *b.* 65·80 at 18°·2 *c.* 66·00 at 18°·1	65·36 at 18°·1

We could not draw a wire of pure copper with only traces of lead in it, for it makes the copper to all appearance perfectly rotten; in GMELIN'S 'Chemistry' it is also stated that copper which contains even 0·1 per cent. of lead cannot either be drawn into fine wire or rolled into thin sheets. Now the copper smelters add a small quantity of lead to their copper, to soften and render it more tough. The addition of lead is supposed to reduce the suboxide of copper present; but, according to J. NAPIER'S* analysis, lead was always found present where it had been added, and often in quantities equal to the amount which had been put in. We have therefore made a few experiments in this direction.

To copper fused in contact with air 0·1 per cent. of lead or tin was added, and the alloy fused in the tobacco-pipe in a current of carbonic acid gas.

		Means.
I. The copper employed conducted	*a.* 83·44 at 13°·0 *b.* 84·45 at 13°·6	83·94 at 13°·3
II. With addition of 0·1 per cent. of tin.	*a.* 90·00 at 14°·0 *b.* 89·80 at 14°·0	89·90 at 14°·0
III. The same repeated	*a.* 91·27 at 13°·8 *b.* 90·65 at 14°·0	90·96 at 13°·9
IV. With addition of 0·1 per cent. of lead	*a.* 89·55 at 12°·0 *b.* 89·42 at 13°·8	89·48 at 12°·9

* Philosophical Magazine, S. 4. vol. v. p. 488.

The quantity of lead and tin remaining was so small that it was not possible to determine it quantitatively.

The experiments, however, tend to prove that on the addition of traces of lead, &c. to copper containing suboxide, a relatively purer metal is obtained.

From the foregoing experiments, we may conclude that *there is no alloy of copper which conducts electricity better than pure copper*; and in conclusion, in order to be able to compare their results with those of others, we would call the attention of experimenters—

I. To the importance of stating whether the wires experimented with are hard drawn or annealed, as it makes in some cases a very marked difference in the values obtained.

II. To the influence of temperature on the conducting power. We find in very few cases the temperature stated at which the observations have been made.

VI. *On the Equation of Differences for an Equation of any Order, and in particular for the Equations of the Orders Two, Three, Four, and Five.* By Arthur Cayley, *Esq., F.R.S.*

Received March 2,—Read March 29, 1860.

The term, *equation of differences*, denotes the equation for the squared differences of the roots of a given equation; the equation of differences afforded a means of determining the number of real roots, and also limits for the real roots, of a given numerical equation, and was upon this account long ago sought for by geometers. In the Philosophical Transactions for 1763, Waring gives, but without demonstration or indication of the mode of obtaining it, the equation of differences for an equation of the fifth order wanting the second term: the result was probably obtained by the method of symmetric functions. This method is employed in the 'Meditationes Algebraicæ' (1782), where the equation of differences is given for the equations of the third and fourth orders wanting the second terms; and in p. 85 the before-mentioned result for the equation of the fifth order wanting the second term, is reproduced. The formulæ for obtaining by this method the equation of differences, are fully developed by Lagrange in the 'Traité des Equations Numériques' (1808); and he finds by means of them the equation of differences for the equations of the orders two and three, and for the equation of the fourth order wanting the second term; and in Note III. he gives, after Waring, the result for the equation of the fifth order wanting the second term. It occurred to me that the equation of differences could be most easily calculated by the following method. The coefficients of the equation of differences, *quà* functions of the differences of the roots of the given equation, are leading coefficients of covariants, or (to use a shorter expression) they are "Seminvariants*," that is, each of them is a function of the coefficients which is reduced to zero by one of the two operators which reduce an invariant to zero. In virtue of this property they can be calculated, when their values are known for the particular case in which one of the coefficients of the given equation is zero. To fix the ideas, let the given equation be $(*\,v, 1)^n=0$; then, when the last coefficient or constant term vanishes, the equation breaks up into $v=0$ and into an equation of the degree $(n-1)$, which I call the reduced equation; the equation of differences will break up into two equations, one of which is the equation of differences for the reduced equation, the other is the equation for the squares of the roots of the same reduced equation. This hardly requires a proof; let the roots of the given equation be α, β, γ, δ, &c., those of the equation of differences are $(\alpha-\beta)^2$, $(\alpha-\gamma)^2$, $(\alpha-\delta)^2$, &c., $(\beta-\gamma)^2$, $(\beta-\delta)^2$, $(\gamma-\delta)^2$, &c.; but in putting the constant term equal to zero, we in effect put one of the roots, say α,

* The term "Seminvariant" seems to me preferable to M. Brioschi's term "Peninvariant."

equal to zero; the roots of the equation of differences thus become β^2, γ^2, δ^2, &c., $(\beta-\gamma)^2$, $(\beta-\delta)^2$, $(\gamma-\delta)^2$, &c. The equation for the squares of the roots can be found without the slightest difficulty; hence if the equation of differences for the reduced equation of the order $(n-1)$ is known, we can, by combining it with the equation for the squares of the roots, form the equation of differences for the given equation with the constant term put equal to zero, and thence by the above-mentioned property of the Seminvariancy of the coefficients, find the equation of differences for the given equation. The present memoir shows the application of the process to equations of the orders two, three, four, and five: part of the calculation for the equation of the fifth order was kindly performed for me by the Rev. R. HARLEY. It is to be noticed that the best course is to apply the method in the first instance to the forms $(a, b, ..\Chi v, 1)^n=0$, without numerical coefficients (or, as they may be termed, the *denumerate forms*), and to pass from the results so obtained to those which belong to the forms $(a, b, ..\Chi v, 1)^n=0$, or *standard forms*. The equation of differences, for $(\alpha-\beta)^2$, &c., the coefficients of which are seminvariants, naturally leads to the consideration of a more general equation having for its roots $(\alpha-\beta)^2\,(x-\gamma y)^2\,(x-\delta y)^2$, &c., the coefficients of which are covariants; and in fact, when, as for equations of the orders two, three, and four, all the covariants are known, such covariant equation can be at once formed from the equation of differences; for equations of the fifth order, however, where the covariants are not calculated beyond a certain degree, only a few of the coefficients of the covariant equation can be thus at once formed. At the conclusion of the memoir, I show how the equation of differences for an equation of the order n can be obtained by the elimination of a single quantity from two equations each of the order $n-1$; and by applying to these two equations the simplification which I have made in BEZOUT'S abridged method of elimination, I exhibit the equation of differences for the given equation of the order n, in a compendious form by means of a determinant; the first-mentioned method is, however, that which is best adapted for the actual development of the equation of differences for the equation of a given order.

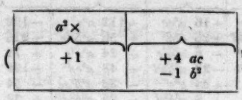
The equations successively considered are

$$(a, b, c \quad \Chi v, 1)^3=0,$$
$$(a, b, c, d \quad \Chi v, 1)^3=0,$$
$$(a, b, c, d, e \quad \Chi v, 1)^4=0,$$
$$(a, b, c, d, e, f\,\Chi v, 1)^5=0.$$

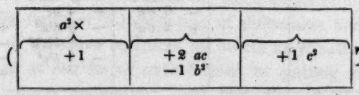
The equation of differences for the quadric, and that for the squares of the roots, are considered to be known, and the other results are derived from them: it will be convenient to write down in the first instance the results for the quadric, the cubic, and the quartic equations, and then explain the process of obtaining them.

For the quadric equation,

Equation of differences is, 0=

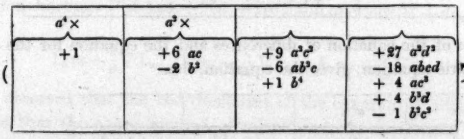


Equation for the squares of the roots is, 0=

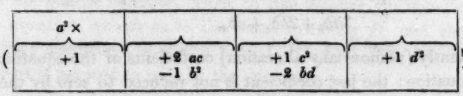


For the cubic equation,

Equation of differences is, 0=



Equation for the squares of the roots is, 0=



For the quartic equation,

Equation of differences is, $0=$

$a^6\times$	$a^4\times$	$a^2\times$				
$+1$	$+8\ ac$ $-3\ b^2$	$+\ 8\ a^3e$ $-\ 2\ a^2bd$ $+22\ a^2c^2$ $-16\ ab^2c$ $+\ 3\ b^4$	$+16\ a^4ce$ $+26\ a^4d^2$ $-\ 6\ a^3b^2e$ $-30\ a^3bcd$ $+28\ a^3c^3$ $+\ 8\ a^2b^2d$ $-24\ a^2b^2c^2$ $+\ 8\ ab^4c$ $-\ 1\ b^6$	$-112\ a^4e^2$ $+\ 56\ a^3bde$ $+\ 24\ a^3c^2e$ $+\ 48\ a^2cd^2$ $-\ 32\ a^2b^2ce$ $-\ 25\ a^2b^2d^2$ $-\ 54\ a^2bc^2d$ $+\ 17\ a^2c^4$ $+\ 6\ ab^4e$ $+\ 38\ ab^3cd$ $-\ 12\ ab^2c^3$ $-\ 6\ b^6d$ $+\ 2\ b^4c^2$	$-192\ a^3ce^2$ $+216\ a^3d^2e$ $+\ 72\ a^2b^2e^2$ $-120\ a^2bcde$ $-\ 54\ a^2bd^3$ $+\ 32\ a^2c^2e$ $+\ 18\ a^2c^2d^2$ $+\ 18\ ab^3de$ $-\ 6\ ab^3c^2e$ $+\ 42\ ab^2cd^2$ $-\ 26\ abc^3d$ $+\ 4\ ac^5$ $-\ 9\ b^4d^2$ $+\ 6\ b^4c^2d$ $-\ 1\ b^4c^4$	$+256\ a^3e^3$ $-192\ a^2bde^2$ $-128\ a^2c^2e^2$ $+144\ a^2cd^2e$ $-\ 27\ a^2d^4$ $+144\ ab^2ce^2$ $-\ 6\ ab^2d^2e$ $-\ 80\ abc^2de$ $+\ 18\ abcd^3$ $+\ 16\ ac^4e$ $-\ 4\ ac^3d^2$ $-\ 27\ b^4e^2$ $+\ 18\ b^2cde$ $-\ 4\ b^2d^3$ $-\ 4\ b^2c^3e$ $+\ 1\ b^2c^2d^2$

$$(\ \ \ \

and consequently

$$L_1 = -\frac{1}{c}\nabla' L_0,\quad L_2 = -\frac{1}{2c}\nabla' L_1,\quad L_3 = -\frac{1}{3c}\nabla' L_2,\quad \&c.,$$

giving

$$L_1 = -\frac{1}{c}\{(-6+24=)18abc^2 - 4b^3c\} = -18abc + 4b^3,$$

$$L_2 = -\frac{1}{2c}\{-54a^2c + (36-36=)0\, ab^2\} = +27a^2,$$

$$L_3 = 0,\ \&c.,$$

and consequently for the last coefficient the value above written down; it will be presently seen how in more complicated cases the calculations should be arranged.

Again, multiplying together the equation of differences and the equation for the squares of the roots of the cubic equation, we obtain an equation which it is not necessary to write down, as it can be at once formed by putting $e=0$ in the equation of differences for the quartic equation. And from the equation so obtained, by the adjunction of the terms in e, we find the equation of differences for the quartic equation, viz. each coefficient is of the form $L_0 + L_1 e + L_2 e^2 +$ &c., where L_0 is known, and such coefficient is reduced to zero by the operator

$$4a\partial_b + 3b\partial_c + 2c\partial_d + d\partial_e;$$

or putting for shortness $\nabla' = 4a\partial_b + 3b\partial_c + 2c\partial_d$, the operator $\nabla' + d\partial_e$. We have therefore

$$L_1 = -\frac{1}{d}\nabla' L_0,\quad L_2 = -\frac{1}{2d}\nabla' L_1,\quad L_3 = -\frac{1}{3d}\nabla' L_2,\quad \&c.$$

It is to be observed that the last coefficient of the equation of differences is the discriminant, and that the above method of calculating the coefficients of the equation of differences, as applied to the last coefficient, is nothing else than the method of calculating the discriminant given in my Fourth Memoir on Quantics.

The multiplication of the equation of differences, and the equation for the squares of the roots of the quartic equation, gives, in like manner, the equation of differences for the quintic equation, except as to the terms involving f; and these are obtained as above, viz. each coefficient is of the form $L_0 + L_1 f + L_2 f^2 +$ &c., where L_0 is known; such coefficient is reduced to zero by the operator

$$5a\partial_b + 4b\partial_c + 3c\partial_d + 2d\partial_e + e\partial_f;$$

or putting for shortness $\nabla' = 5a\partial_b + 4b\partial_c + 3c\partial_d + 2d\partial_e$, the operator $\nabla' + e\partial_f$. We have, therefore,

$$L_1 = -\frac{1}{e}\nabla' L_0,\quad L_2 = -\frac{1}{2e}\nabla' L_1,\quad L_3 = -\frac{1}{3e}\nabla' L_2,\ \&c.,$$

which give L_1, L_2, &c. by means of L_0. For the calculation of $\nabla' L$ (where L is any one of the coefficients L_0, L_1, &c.), it is proper to separate the terms involving

the different powers of e, and write $L=M_0+M_1e+M_2e^2+$ &c., $\nabla'=\nabla''+2d\partial_e$, where $\nabla''=5a\partial_a+4b\partial_c+3c\partial_d$. We have then

$$\nabla L= \begin{array}{l|l|l} \nabla''M_0+ e & \nabla''M_1+ e^2 & \nabla''M_2+ \text{\&c.}, \\ +2dM_1 & +4dM_2 & +6dM_3, \end{array}$$

or, what is the same thing,

$$\frac{1}{e}\nabla L= \begin{array}{l|l} \nabla''M_1+ e & \nabla''M_2+\cdots \\ +4dM_2 & +4dM_3; \end{array}$$

and as an equation which should be satisfied identically, and which would therefore serve as a verification,

$$\nabla''M_0+2dM_1=0;$$

but as a verification was obtained by other means, the equations of this kind were not used for the purpose. It may be interesting to give the actual calculation of one of the coefficients, say of coefficient θ^3 (which, with coefficient θ, was calculated by Mr. Harley).

Calculation of coefficient θ^2 in equation of differences for the quintic equation

$$(a, b, c, d, e, f\chi v, 1)^5 = 0.$$

Calculation of L_0.

	$2ae$	$-2bd$	$+c^2$	$2ce$	$-d^2$	e^2		In eq. of diff. for quartic.
	Coeff. θ^0.			Coeff. θ^1.		Coeff. θ^2.		
a^4e^4	+512					−112	=	+400
a^3bde^3	−384	−512				+ 56		−840
$a^3c^2e^3$	−256		+256	−384		+ 24		−360
$a^3cd^2e^3$	+288			+432	+192	+ 48		+960
a^3d^4e	− 54				−216			−270
$a^2b^2ce^3$	+288			+144		− 32		+400
$a^2b^2d^2e^2$	− 12	+384			− 72	− 25		+275
$a^2bc^2de^2$	−160	+256	−192	−240		− 54		−390
a^2bcd^3e	+ 36	−288		−108	+120			−240
abd^5		+ 54			+ 54			+108
$a^2c^3e^3$	+ 32		−128	+ 64		+ 17		− 15
$a^2c^2d^2e$	− 8		+144	+ 36	− 32			+140
$a^2c^3d^4$			− 27		− 18			− 45
ab^3e^3	− 54					+ 6		− 48
ab^2cde^2	+ 36	−288		+ 36		+ 38		−178
ab^2d^3e	− 8	+ 12			− 18			− 14
$ab^2c^2e^2$	− 8		+144	− 12		− 12		+112
$ab^2c^2d^3e$	+ 2	+160	− 6	+ 84	+ 6			+246
ab^2cd^4		− 36			− 42			− 78
abc^3de		− 32	− 80	− 52				−164
abc^2d^3		+ 8	+ 18		+ 26			+ 52
ac^5e			+ 16	+ 8				+ 24
ac^3d^2			− 4		− 4			− 8
b^4de^3		+ 54				− 6		+ 48
$b^4c^2e^2$			− 27			+ 2		− 25
b^4cd^2e		− 36		− 18				− 54
b^4d^4		+ 8			+ 9			+ 17
b^3c^3de		+ 8	+ 18	+ 12				+ 38
$b^3c^3d^3$		− 2	− 4		− 6			− 12
b^3c^4e			− 4	− 2				− 6
$b^2c^4d^2$			+ 1		+ 1			+ 2

$L_0 = A + Be + Ce^2 + De^3 + Ee^4$, suppose, then,

$-B=$	$-C=$	$-D=$	$-E=$
a^2d^3 +270	a^3cd^2 −960	a^3bd +840	a^4 −400
a^3bcd^3 +240	$a^3b^2d^2$ −275	a^3c^3 +360	
$a^3c^2d^2$ −140	a^2bc^2d +390	a^2b^2e −400	
ab^3d^3 + 14	a^3c^4 + 15	ab^4 + 48	
$ab^2c^3d^2$ −246	ab^3cd +178		
abc^4d +164	ab^3c^3 −112		
ac^6 − 24	b^5d − 48		
b^4cd^2 + 54	b^4c^2 + 25		
b^3c^3d − 38			
b^2c^5 + 6			

Calculation of L_1.

Terms of $L_1 f$ not involving e.

$-f(\nabla''B+4dC)$ viz.	$5a\partial_b$	$+4b\partial_c$	$+3c\partial_d$	$4d$		
		$-B$		$-C$		
a^3cd^3f	$+1200$		$+3240$	-3840	$=$	$+600$
$a^2b^2d^2f$	$+210$	$+960$		-1100		$+70$
$a^2bc^2d^2f$	-2460	-1680	$+2160$	$+1560$		-420
a^2c^4df	$+820$		-840	$+60$		$+40$
ab^3cd^2f	$+1080$	-1968	$+126$	$+712$		-50
ab^2c^2df	-570	$+2624$	-1476	-448		$+130$
abc^3f	$+60$	-576	$+492$			-24
b^4d^2f		$+216$		-192		$+24$
b^3c^2df		-456	$+324$	$+100$		-32
b^2c^3f		$+120$	-114			$+6$

Terms of $L_1 f$ involving e^1.

$-ef(\nabla''C+6dD)$ viz.	$5a\partial_b$	$+4b\partial_c$	$+3c\partial_d$	$6d$		
		$-C$		$-D$		
a^3bd^2ef	-2750	-3840		$+5040$	$=$	-1550
a^3c^2def	$+1950$		-5760	$+2160$		-1650
a^2b^2cdef	$+2670$	$+3120$	-1650	-2400		$+1740$
a^2bc^2ef	-1120	$+240$	$+1170$			$+290$
ab^4def	-1200	$+712$		$+288$		-200
ab^3c^2ef	$+500$	-1344	$+534$			-310
b^3cef		$+200$	-144			$+56$

Terms of $L_1 f$ involving e^2.

$-e^2f(\nabla''D+8dE)$ viz.	$5a\partial_b$	$4b\partial_c$	$3c\partial_d$	$8d$		
		$-D$		$-E$		
a^4de^2f	$+4200$			-3200	$=$	$+1000$
a^3bce^2f	-4000	$+2880$	$+2520$			$+1400$
$a^2b^2e^2f$	$+960$	-1600				-640

Calculation of L_2.

$L_1 = A + Be + Ce^2$, suppose, where

$-\frac{1}{2}B=$		$-\frac{1}{2}C=$	
a^3bd^2	$+775$	a^4d	-500
a^3c^2d	$+825$	a^3bc	-700
a^2b^2cd	-870	a^2b^3	$+320$
a^2bc^3	-145		
ab^4d	$+100$		
ab^3c^2	$+155$		
b^4c	-28		

Terms of $L_3 f^3$ not involving e.

$-f^3(\nabla''\frac{1}{2}B+4d\frac{1}{2}C)$ viz.	$5a\partial_b$	$4b\partial_c$	$3c\partial_d$	$4d$	
		$-\frac{1}{2}B$		$-\frac{1}{2}C$	
$a^4d^2f^2$	+3875			−2000 =	+1875
a^3bcdf^2	−8700	+6600	+4650	−2800	− 250
$a^2c^2f^2$	− 725		+2475		+1750
$a^2b^2df^2$	+2000	−3480		+1280	− 200
$a^2b^2c^2f^2$	+2325	−1740	−2610		−2025
ab^4cf^2	− 700	+1240	+ 300		+ 840
ab^5f^2		− 112			− 112

Terms of $L_3 f^3$ involving e^1.

$-ef^2\nabla''\frac{1}{2}C$ viz.	$5a\partial_b$	$4b\partial_c$	$3c\partial_d$	
		$-\frac{1}{2}C$		
a^4cef^2	−3500		−1500 =	−5000
$a^3b^2ef^2$	+4800	−2800		+2000

Calculation of L_3 (gives $L_3=0$).

$$L_3=A+Be,$$

$-\frac{1}{3}B=$	
a^4c	$+1666\frac{2}{3}$
a^3b^2	$-666\frac{2}{3}$

Terms of $L_3 f^3$.

$-f^3\nabla''\frac{1}{3}B$ viz.	$5a\partial_b$	$4b\partial_c$	$3c\partial_d$	
		$-\frac{1}{3}B$		
a^4bf^3		$-6666\frac{2}{3}$ $+6666\frac{2}{3}$	=	0

And the required coefficient of θ^3 is

$$L_0+L_1f+L_2f^2.$$

All the coefficients were calculated in this manner, except the last coefficient, which was deduced from the known value of the discriminant for the standard form. And we have thus the complete expression of the equation of differences for the general quintic equation under the denumerate form $(a, b, c, d, e, f)(v, 1)^5=0$, viz.—

Equation of differences for $(a, b, c, d, e, f^{\nabla}(v, 1)^5 = 0$ is

δ^{10}	δ^9	δ^8	δ^7	δ^6	δ^5	δ^4
$a^5\times$	$a^4\times$	$a^3\times$	$a^2\times$			
$+1$	$+10\ ae$	$+10\ a^3e$	$+50\ a^4ce$	$+200\ a^4df$	$+625\ a^4f^2$	$+1750\ a^3cf^2$
	$-\ 4\ b^2$	$-\ 4\ a^2bd$	$+25\ a^4d^2$	$-\ 95\ a^3e^2$	$-250\ a^3bef$	$-\ 950\ a^3def$
		$+39\ a^2c^2$	$-20\ a^3b^2e$	$-120\ a^2bcf$	$+400\ a^3cdf$	$+\ 40\ a^3e^3$
		$-30\ ab^2c$	$-50\ a^3bcd$	$+\ 36\ a^2bde$	$-360\ a^2ce^2$	$-\ 130\ a^2beef$
		$+\ 6\ b^4$	$+80\ a^3c^3$	$+124\ a^2c^2e$	$+260\ a^2d^2e$	$-\ 700\ a^2b^2f^2$
			$+16\ a^2b^2d$	$+\ 92\ a^2cd^2$	$-110\ a^2b^2df$	$+\ 142\ a^2bde^2$
			$-81\ a^2b^2c^2$	$+\ 32\ a^2b^2f$	$+169\ a^2b^2e^2$	$+\ 380\ a^2bd^2f$
			$+30\ ab^4c$	$-\ 98\ a^2b^2ce$	$-240\ a^2b^2cf$	$-\ 522\ a^2c^2e^2$
			$-\ 4\ b^6$	$-\ 44\ a^2b^2d^2$	$-104\ a^2bcde$	$+\ 240\ a^2c^2df$
				$-160\ a^2bc^2d$	$-104\ a^2bd^2e$	$+\ 708\ a^2cd^2e$
				$+\ 95\ a^2c^4$	$+196\ a^2c^2e$	$-\ 53\ a^2d^4$
				$+\ 18\ a^2b^4e$	$+118\ a^2c^2d^2$	$+\ 128\ a^2b^2ef$
				$+116\ a^2b^2cd$	$+150\ a^2b^2cf$	$+\ 388\ a^2b^2ce^2$
				$-104\ a^2b^2c^3$	$-\ 10\ a^2b^2de$	$-\ 394\ a^2b^2cdf$
				$-\ 20\ a^2b^2d$	$-180\ a^2b^2c^2e$	$-\ 378\ a^2b^2d^2e$
				$+\ 45\ a^2b^4c^2$	$+\ 20\ a^2b^2cd^2$	$-\ 144\ a^2bc^2f$
				$-\ 10\ ab^6c$	$-220\ a^2bc^3d$	$-\ 480\ a^2bc^2de$
				$+\ 1\ b^8$	$+\ 66\ a^2c^5$	$-\ 156\ a^2bcd^3$
					$-\ 24\ a^2b^2f$	$+\ 194\ a^2c^4e$
					$+\ 66\ a^2b^2ce$	$+\ 52\ a^2c^3d^2$
					$-\ 3\ a^2b^4d^2$	$+\ 66\ a^2b^2df$
					$+192\ a^2b^2c^2d$	$-\ 84\ a^2b^4e^2$
					$-\ 66\ a^2b^2c^4$	$+\ 194\ a^2b^2c^2f$
					$-\ 8\ ab^6e$	$+\ 330\ a^2b^2cde$
					$-\ 66\ ab^4cd$	$+\ 92\ a^2b^2d^2$
					$+\ 24\ ab^4c^3$	$-\ 152\ a^2b^2c^2e$
					$+\ 8\ b^6d$	$+\ 174\ a^2b^2c^2d^2$
					$-\ 3\ b^6c^2$	$-\ 140\ a^2bc^4d$
						$+\ 25\ a^2c^6$
						$-\ 70\ ab^4cf$
						$-\ 42\ ab^4de$
						$+\ 32\ ab^4c^2e$
						$-\ 144\ ab^4cd^2$
						$+\ 100\ ab^4c^2d$
						$-\ 18\ ab^2c^3$
						$+\ 8\ b^6f$
						$-\ 2\ b^6ce$
						$+\ 22\ b^6d^2$
						$-\ 16\ b^6c^2d$
						$+\ 3\ b^6c^4$

$(\mathfrak{Y}(\theta, 1)^{10} = 0$, viz. the function in $\mathfrak{S}$ is

θ^3.	θ^2.	θ.	θ^0.
$-3750\ a^4ef^2$	$-5000\ a^4cef^2$	$-6250\ a^4df^3$	$+3125\ a^4f^4$
$+1500\ a^4bdf^2$	$+1875\ a^4d^2f^2$	$+5000\ a^4e^2f^2$	$-2500\ a^4bef^3$
$+1500\ a^4be^2f$	$+1000\ a^4de^2f$	$+3750\ a^3bef^3$	$-3750\ a^3cdf^3$
$+2500\ a^4e^2f^2$	$+\ 400\ a^4e^4$	$-\ 250\ a^3bde^2f^2$	$+2000\ a^3ce^2f^2$
$-2150\ a^4cdef$	$+2000\ a^3b^2ef^3$	$-2000\ a^3b^2f$	$+2250\ a^3d^2ef^2$
$-\ 80\ a^4ce^3$	$-\ 250\ a^3bcdf^2$	$-3750\ a^3c^2ef^2$	$-1600\ a^3de^2f$
$+\ 700\ a^4d^2f$	$+1400\ a^3bce^2f$	$+3000\ a^2cd^2f^2$	$+\ 256\ a^3e^4$
$+\ 570\ a^4d^2e^2$	$-1550\ a^3bd^2ef$	$+\ 200\ a^2cde^2f$	$+2000\ a^2b^2df^3$
$-\ 40\ a^3b^2def$	$-\ 840\ a^3bde^3$	$+\ 320\ a^2ce^4$	$-\ 50\ a^2b^2e^2f^2$
$-2450\ a^3b^2ef^2$	$+1750\ a^3c^2f^2$	$-\ 450\ a^2d^2ef$	$+2250\ a^2bc^2f^3$
$-\ 118\ a^3b^2e^3$	$-1650\ a^3c^2def$	$-\ 40\ a^2d^2e^3$	$-2050\ a^2bcdef^2$
$+\ 290\ a^2bc^2ef$	$-\ 360\ a^3c^2e^3$	$-1000\ a^2b^3f^3$	$+\ 160\ a^2bce^2f$
$-\ 400\ a^2bcd^2f$	$+\ 600\ a^2cd^2f$	$+1950\ a^2b^2cef^2$	$-\ 900\ a^2bd^2f^2$
$-\ 158\ a^2bcde^2$	$+\ 960\ a^2cd^2e^2$	$-1150\ a^2b^2d^2f^2$	$+1020\ a^2bd^2e^2f$
$-\ 596\ a^2bd^2ef$	$-\ 270\ a^2d^2e$	$+1170\ a^2b^2def^2$	$-\ 192\ a^2bde^3$
$+\ 80\ a^2c^2df$	$-\ 200\ a^2b^2df^3$	$+\ 72\ a^2b^2e^4$	$-\ 900\ a^2c^2ef^2$
$-\ 308\ a^2c^2e^2$	$-\ 640\ a^2b^2e^2f$	$-2100\ a^2bc^2df^2$	$+\ 825\ a^2c^2d^2f^2$
$+\ 612\ a^2c^2d^2e$	$-2025\ a^2b^2cf^3$	$+1380\ a^2bc^2ef$	$+\ 560\ a^2c^2de^2f$
$-\ 102\ a^2cd^4$	$+1740\ a^2b^2cdef$	$-\ 550\ a^2bcd^2ef$	$-\ 128\ a^2c^2e^4$
$+\ 490\ a^2b^4f^2$	$+\ 400\ a^2b^2ce^3$	$-\ 504\ a^2bcde^3$	$-\ 630\ a^2cd^3ef$
$+\ 180\ a^2b^3cef$	$+\ 70\ a^2b^2d^3f$	$+\ 180\ a^2bd^4f$	$+\ 144\ a^2cd^2e^3$
$+\ 112\ a^2b^2d^2f$	$+\ 275\ a^2b^2d^2e^2$	$+\ 138\ a^2bd^3e^2$	$+\ 108\ a^2d^4f$
$+\ 92\ a^2b^2de^2$	$+\ 290\ a^2bc^2ef$	$+\ 675\ a^2c^4f^2$	$-\ 27\ a^2d^4e^2$
$+\ 86\ a^2b^2c^2df$	$-\ 420\ a^2bc^2d^2f$	$-\ 330\ a^2c^3def$	$-1600\ ab^2ef^3$
$+\ 388\ a^2b^2c^2e^2$	$-\ 390\ a^2bc^2de^2$	$-\ 224\ a^2c^3e^3$	$+\ 160\ ab^2def^2$
$+\ 150\ a^2b^2cd^2e$	$-\ 240\ a^2bcd^3e$	$+\ 60\ a^2c^2d^2f$	$-\ 36\ ab^2e^3f$
$+\ 160\ a^2b^2d^4$	$+\ 108\ a^2bd^4$	$+\ 434\ a^2c^2d^2e^2$	$+1020\ ab^2c^2ef^2$
$-\ 48\ a^2bc^4f$	$+\ 40\ a^2c^4df$	$-\ 198\ a^2cd^3e$	$+\ 560\ ab^2cd^2f^2$
$+\ 504\ a^2bc^3de$	$-\ 15\ a^2c^4e^2$	$+\ 27\ a^2d^5$	$+\ 144\ ab^2cde^2f$ $\mathfrak{Y}(\theta, 1)^{10}$
$+\ 106\ a^2c^3e$	$+\ 140\ a^2c^3d^2e$	$-\ 240\ ab^4ef^2$	$+\ 144\ ab^2ce^4$
$-\ 7\ a^2c^4d^2$	$-\ 45\ a^2c^2d^4$	$+1320\ ab^3cdf^2$	$+\ 24\ ab^2d^2ef$
$-\ 68\ ab^4ef$	$+\ 840\ ab^4ef^2$	$-1230\ ab^3ce^2f$	$-\ 6\ ab^2d^2e^3$
$-\ 86\ ab^4cdf$	$-\ 200\ ab^4def$	$-\ 12\ ab^3d^2ef$	$-\ 630\ abc^2df^2$
$-\ 178\ ab^4ce^2$	$-\ 48\ ab^4e^3$	$+\ 18\ ab^3de^3$	$+\ 24\ abc^2e^2f$
$-\ 54\ ab^4d^2e$	$-\ 310\ ab^3c^2ef$	$-\ 450\ ab^3c^2f^2$	$+\ 356\ abc^2d^2ef$
$+\ 234\ ab^3c^2de$	$-\ 50\ ab^3cd^3f$	$+\ 594\ ab^3c^2def$	$-\ 80\ abc^2de^3$
$+\ 34\ ab^3c^2f$	$-\ 178\ ab^3cde^2$	$+\ 282\ ab^3c^2e^3$	$-\ 72\ abcd^3f$
$-\ 148\ ab^3cd^3$	$-\ 14\ ab^3d^3e$	$-\ 154\ ab^2cd^2f$	$+\ 18\ abcd^3e^2$
$-\ 56\ ab^2c^4e$	$+\ 130\ ab^2c^2df$	$-\ 114\ ab^2cd^2e^2$	$+\ 108\ ac^4f^2$
$+\ 112\ ab^2c^3d^2$	$+\ 112\ ab^2c^2e^3$	$+\ 6\ ab^2d^4e$	$-\ 72\ ac^4def$
$-\ 34\ abc^4d$	$+\ 246\ ab^2c^2d^2e$	$-\ 72\ abc^4ef$	$+\ 16\ ac^4e^3$
$+\ 4\ ac^5$	$-\ 78\ ab^2cd^4$	$+\ 24\ abc^3d^2f$	$+\ 16\ ac^3d^2f$
$+\ 16\ b^4df$	$-\ 24\ abc^3f$	$-\ 186\ abc^3de^2$	$-\ 4\ ac^3d^2e^3$
$+\ 26\ b^4e^2$	$-\ 164\ abc^3de$	$+\ 116\ abc^2d^3e$	$+\ 256\ b^5f^3$
$-\ 6\ b^4e^2f$	$+\ 52\ abc^2d^3$	$-\ 18\ abcd^4$	$-\ 192\ b^4cef^2$
$-\ 30\ b^4cde$	$+\ 24\ ac^4e$	$+\ 36\ ac^4e^3$	$-\ 128\ b^4d^2f^2$
$+\ 28\ b^4d^3$	$-\ 8\ ac^3d^2$	$-\ 24\ ac^4d^2e$	$+\ 144\ b^4def^2$
$+\ 8\ b^4c^2e$	$-\ 112\ b^5f^2$	$+\ 4\ ac^3d^4$	$-\ 27\ b^4e^4$
$-\ 24\ b^4c^2d^2$	$+\ 56\ b^5cef$	$-\ 192\ b^4df^3$	$+\ 144\ b^3c^2df^2$
$+\ 8\ b^3c^4d$	$+\ 24\ b^5d^2f$	$+\ 216\ b^4c^2f^2$	$-\ 6\ b^3c^2e^2f$
$-\ 1\ b^3c^6$	$+\ 48\ b^5de^2$	$+\ 72\ b^4c^2ef^2$	$-\ 80\ b^3cd^2ef^2$
	$-\ 32\ b^4c^2df$	$-\ 120\ b^4cdef$	$+\ 18\ b^3cde^3$
	$-\ 25\ b^4c^2e^2$	$-\ 54\ b^4ce^3$	$+\ 16\ b^3d^4f$
	$-\ 54\ b^4cd^2e$	$+\ 32\ b^4d^3f$	$-\ 4\ b^3d^3e^2$
	$+\ 17\ b^4d^4$	$+\ 18\ b^4d^2e^2$	$-\ 27\ b^3c^4f^2$
	$+\ 6\ b^3c^4f$	$+\ 18\ b^3c^2ef$	$+\ 18\ b^3c^2def$
	$+\ 38\ b^3c^3de$	$-\ 6\ b^3c^2d^2f$	$-\ 4\ b^3c^2e^3$
	$-\ 12\ b^3c^2d^3$	$+\ 42\ b^3c^2de^2$	$-\ 4\ b^3c^2d^2f$
	$-\ 6\ b^3c^4e$	$-\ 26\ b^3cd^3e$	$+\ 1\ b^3c^2d^2e^2$
	$+\ 2\ b^3c^4d^2$	$+\ 4\ b^3d^5$	
		$-\ 9\ b^2c^4e^2$	
		$+\ 6\ b^3c^3d^2e$	
		$-\ 1\ b^3c^3d^4$	

It may be remarked, that if ω is an imaginary cube root of unity, then the roots of the equation $(1, 1, 1, 1, 1, 1)(v, 1)^5=0$ are $-1, \omega, \omega^2, -\omega, -\omega^2$; the differences of the roots are

$$\begin{aligned} &-1-\omega,\ -1-\omega^2,\ -1+\omega,\ -1+\omega^2,\ \omega-\omega^2,\ 2\omega,\ \omega+\omega^2,\ \omega^2+\omega,\ 2\omega^2,\ -\omega+\omega^2 \\ =\ &\omega^2,\ \ \omega,\ -1+\omega,\ -1+\omega^2,\ \omega-\omega^2,\ 2\omega,\ -1,\ -1,\ 2\omega^2,\ -\omega+\omega^2, \end{aligned}$$

and the squares of the differences are

$$\omega,\ \omega^2,\ -3\omega,\ -3\omega^2,\ -3,\ 4\omega^2,\ 1,\ 1,\ 4\omega,\ -3,$$

from which the equation of differences is found to be

$$(\theta^2+\theta+1)(\theta^2-3\theta+9)(\theta^2+4\theta+16)(\theta^2-2\theta+1)(\theta^2+6\theta+9)=0;$$

or multiplying out, it is

$$(1, 6, 21, 46, 108, 546, 493, -1410, -567, -540, +1296)(\theta, 1)^{10}=0;$$

which is what the preceding expression of the equation of differences becomes upon writing therein $a=b=c=d=e=f=1$. Moreover, upon passing (as will presently be done) to the standard form, and then writing $a=b=c=d=e=f=1$, all the coefficients (except the first coefficient, which is equal to unity) should become equal to zero; these two tests afford a complete verification of the result.

The following corrections have to be made in WARING's result, as given by himself and LAGRANGE (WARING, Phil. Trans. 1763):—

WARING, Meditationes Algebraicæ, p. 85:—

for $+\ 169\, q^3s$ *read* $+196\, q^3s$ (in coefficient w^5).

LAGRANGE, Equations Numériques, p. 108:—

for $+1200$ CE *read* $+200$ CE (in d)
for $-\ 169$ B^{3}D *read* -196 B^{3}D (in e)
for $-\ 25$ B^6 *read* $+\ 25$ B^6 (in f)
for $+\ 27$ C^{4}D^2 *read* $-\ 27$ C^{4}D^2 (in k).

It may be noticed, that if in the coefficients of the several powers of θ (as they are written down in the columns, without regarding the power of a which multiplies the entire column), we attend only to the terms independent of a, we have the series

$$\begin{aligned} 1,\ -4b^3,\ +6b^4,\ -4b^5,\ +1b^6,\ &+8b^7d,\ +\ 8b^7f,\ \text{&c.} \\ &-3b^6c^3,\ -\ 2b^6ce \\ &+22b^6d^2 \\ &-16b^5c^3d \\ &+3b^4c^4, \end{aligned}$$

the law of the first terms of which, up to the term $+1b^6$, is obvious; but the term $+1b^6$, which is the last term of this initial series, is also the first term of a terminal series, the terms of which are deduced from the coefficients in the equation of differences for the

quartic equation $(a, b, c, d, e\text{)}(v, 1)^4=0$, viz. these coefficients are

$a^6\times$	$a^4\times$	$a^2\times$	&c.
$+1$	$+8ac$	$+8a^3e$	
	$-3b^2$	$-2a^2bd$	
		$+22a^2c^2$	
		$-16ab^2c$	
		$+3b^4$;	

and by writing b, c, d, e, f in the place of a, b, c, d, e respectively, and multiplying by b^2, we have the above-mentioned series,

$$+1b^6,\ +8b^7d,\ \&c.$$
$$-3b^8c^2.$$

It is easy to see, *à priori*, in the case of an equation of any order, that this property holds good.

Passing now to the standard forms,—

For the quadric $(a, b, c\text{)}(v, 1)^2=0$, the equation of differences is, $0=$

$a^2\times$	$4\times$
$+1$	$+1\ ac$
	$-1\ b^2$

$(\ \ \ \text{)}(\theta, 1)$.

For the cubic equation $(a, b, c, d\text{)}(v, 1)^3=0$, the equation of differences is, $0=$

$a^4\times$	$18\,a^2\times$	$81\times$	$27\times$
$+1$	$+1\ ac$	$+1\ a^2c^2$	$+1\ a^2d^2$
	$-1\ b^2$	$-2\ ab^2c$	$-6\ abcd$
		$+1\ b^4$	$+4\ ac^3$
			$+4\ b^3d$
			$-3\ b^2c^2$

$(\ \ \ \text{)}(\theta, 1)^3$.

For the quartic equation $(a, b, c, d, e\text{)}(v, 1)^4=0$, the equation of differences is, $0=$

$a^6\times$	$48a^4\times$	$8a^3\times$	$32\times$	$16\times$	$1152\times$	$256\times$
$+1$	$+1\ ac$	$+\ 1\ a^3e$	$\ \ 3\ a^4ce$	$-\ \ 7\ a^4e^2$	$-\ 1\ a^3ce^2$	$+\ \ 1\ a^3e^3$
	$-1\ b^2$	$-\ 4\ a^2bd$	$+\ 13\ a^4d^2$	$+\ 56\ a^3bde$	$+\ 3\ a^3d^2e$	$-\ 12\ a^2bde^2$
		$+\ 99\ a^2c^2$	$-\ \ 3\ a^3b^2e$	$+\ 54\ a^3c^2e$	$+\ 1\ a^2b^2e^2$	$-\ 18\ a^2c^2e^2$
		$-192\ ab^2c$	$-\ 90\ a^3bcd$	$+288\ a^3cd^2$	$-10\ a^2bcde$	$+\ 54\ a^2cd^2e$
		$+\ 96\ b^4$	$+189\ a^3c^3$	$-\ 192\ a^2b^2ce$	$-12\ a^2bd^3$	$-\ 27\ a^2d^4$
			$+\ 64\ a^2b^2d$	$-\ 400\ a^2b^2d^2$	$+\ 6\ a^2c^3e$	$+\ 54\ ab^2ce^2$
			$-432\ a^2b^2c^2$	$-1944\ a^2bc^2d$	$+\ 9\ a^2c^2d^2$	$-\ \ 6\ ab^2d^2e$
			$+384\ ab^4c$	$+1377\ a^2c^4$	$+\ 4\ ab^3de$	$-180\ abc^2de$
			$-128\ b^6$	$+\ \ 96\ ab^4e$	$-\ 3\ ab^2c^2e$	$+108\ abcd^2$
				$+3648\ ab^3cd$	$+56\ ab^2cd^2$	$+\ 81\ ac^4e$
				$-2592\ ab^3c^3$	$-78\ abc^3d$	$-\ 54\ ac^3d^2$
				$-1536\ b^4d$	$+27\ ac^5$	$-\ 27\ b^4e^2$
				$+1152\ b^4c^2$	$-32\ b^4d^2$	$+108\ b^3cde$
					$+48\ b^3c^2d$	$-\ 64\ b^3d^3$
					$-18\ b^2c^3$	$-\ 54\ b^3c^2e$
						$+\ 36\ b^2c^2d^2$

$(\ \ \ \text{)}(\theta, 1)^6$.

For the quintic equation $(a, b, c, d, e, f)(v, 1)^5 = 0$, the equation of differences is,

θ^{10}	θ^9	θ^8	θ^7	θ^6	θ^5	θ^4
$a^5\times$	$100\,a^4\times$	$50\,a^4\times$	$2500\,a^2\times$	$125\times$	$625\times$	$2500\times$
$+1$	$+1\ ac$	$+\ 1\ a^3e$	$+\ 1\ a^4ce$	$+\ 16\ a^5df$	$+\ 1\ a^5f^2$	$+\ 7\ a^5cf^2$
	$-1\ b^2$	$-\ 4\ a^2bd$	$+\ 1\ a^4d^2$	$-\ 19\ a^5e^2$	$-\ 10\ a^5bef$	$-\ 19\ a^5def$
		$+\ 78\ a^2c^2$	$-\ 1\ a^3b^2e$	$-\ 48\ a^4bcf$	$+\ 64\ a^4cdf$	$+\ 2\ a^5e^3$
		$-150\ ab^2c$	$-10\ a^3bcd$	$+\ 72\ a^4bde$	$-\ 144\ a^4ce^2$	$-\ 13\ a^4bcef$
		$+\ 75\ b^4$	$+32\ a^3c^3$	$+\ 496\ a^3c^2e$	$+\ 208\ a^3d^2e$	$-\ 7\ a^4b^2f^2$
			$+\ 8\ a^2b^2d$	$+\ 736\ a^3cd^2$	$-\ 44\ a^3b^2df$	$+\ 71\ a^4bde^2$
			$-81\ a^2b^2c^2$	$+\ 32\ a^3b^2f$	$+\ 169\ a^3b^2e^2$	$+\ 76\ a^4bd^2f$
			$+75\ ab^4c$	$-\ 980\ a^3b^2ce$	$-\ 192\ a^3bc^2f$	$-\ 522\ a^4c^2e^2$
			$-25\ b^6$	$-\ 880\ a^3b^2d^2$	$-\ 416\ a^3bcde$	$+\ 96\ a^4c^2df$
				$-\ 6400\ a^3bc^2d$	$-\ 832\ a^3bd^3$	$+\ 1416\ a^4cd^2e$
				$+\ 7600\ a^3c^4$	$+\ 1568\ a^3c^3e$	$-\ 212\ a^4d^4$
				$+\ 450\ a^2b^4e$	$+\ 1888\ a^3c^2d^2$	$+\ 32\ a^3b^2ef$
				$+11600\ a^2b^2cd$	$+\ 300\ a^2b^3ef$	$+\ 970\ a^3b^2ce^2$
				$-20800\ a^2b^2c^3$	$-\ 100\ a^2b^3de$	$-\ 394\ a^3b^2cdf$
				$-\ 5000\ a^2b^3d$	$-\ 3600\ a^2b^2c^2e$	$-\ 1890\ a^3b^2d^2e$
				$+22500\ a^2b^4c^2$	$+\ 800\ a^2b^2cd^2$	$-\ 288\ a^3bc^2f$
				$-12500\ ab^5c$	$-17600\ a^2bc^3d$	$-\ 4800\ a^3bc^2de$
				$+\ 3125\ b^6$	$+10560\ a^2c^5$	$-\ 3120\ a^3bcd^3$
					$-\ 120\ a^2b^3f$	$+\ 3880\ a^3c^4e$
					$+\ 3300\ a^2b^2cde$	$+\ 2080\ a^3c^3d^2$
					$-\ 300\ a^2b^2d^3$	$+\ 165\ a^2b^4df$
					$+38400\ a^2b^2c^2d$	$-\ 525\ a^2b^4e^2$
					$-26400\ a^2b^2c^4$	$+\ 970\ a^2b^2c^2f$
					$-\ 1000\ ab^5e$	$+\ 8250\ a^2b^2cde$
					$+33000\ ab^4cd$	$+\ 4600\ a^2b^2d^3$
					$+24000\ ab^4c^3$	$-\ 7600\ a^2b^2c^3e$
					$+10000\ b^7d$	$+17400\ a^2b^2c^2d^2$
					$-\ 3750\ b^6c^2$	$-28000\ a^2bc^4d$
						$+10000\ a^2c^6$
						$-\ 875\ ab^5cf$
						$-\ 2625\ ab^5de$
						$+\ 4000\ ab^4c^2e$
						$-36000\ ab^4cd^2$
						$+50000\ ab^3c^3d$
						$-18000\ ab^3c^5$
						$+\ 250\ b^7f$
						$-\ 625\ b^6ce$
						$+13750\ b^6d^2$
						$-20000\ b^5c^3d$
						$+\ 7500\ b^4c^5$

$0=(\mathfrak{Y}\theta, 1)^{10}=0$, viz. the function in $\mathfrak{S}$ is

θ^3.	θ^2.	θ.	θ^0.
$1250\times$	$62500\times$	$62500\times$	$3125\times$
$-3a^1ef^2$	$-4a^1cef^2$	$-1a^1df^3$	$+1a^1f^4$
$+12a^1bdf^3$	$+3a^1d^2f^3$	$+2a^1e^2f^3$	$-20a^2bef^3$
$+30a^2be^2f$	$+4a^1de^2f$	$+3a^2bcf^3$	$-120a^2cdf^3$
$+40a^2c^2f^2$	$+4a^1e^4$	$-1a^2bdef^2$	$+160a^2ce^2f^2$
$-172a^2cdef$	$+4a^2b^2ef^2$	$-20a^2be^2f$	$+360a^2d^2ef^2$
$-16a^2ce^3$	$-2a^2bcdf^3$	$-30a^2c^2ef^2$	$-640a^2de^2f$	$\mathfrak{Y}\theta, 1)^{10}$
$+112a^1d^2f^2$	$+28a^2bce^2f$	$+48a^2cd^2f^2$	$+256a^2e^4$
$+228a^1d^2e^2$	$-62a^2bd^2ef$	$+8a^2cde^2f$	$+160a^3b^2df^3$
$-8a^2b^2def$	$-84a^2bde^3$	$+32a^2c^2e^4$	$-10a^3b^2e^2f^2$
$-98a^2b^2e^2f^2$	$+28a^3c^2f^2$	$-36a^3d^2ef$	$+360a^3bc^2f^2$
$-59a^2b^2e^3$	$-132a^3c^2def$	$-8a^3d^2e^3$	$-1640a^3bcdef^2$
$+116a^2bc^2ef$	$-72a^3c^2e^3$	$-2a^3b^2f^3$	$+320a^3bce^2f$
$-320a^2bcd^2f^2$	$+96a^3ed^2f$	$+39a^3b^2cef^2$	$-1440a^3bd^2f^2$
$-316a^2bcde^2$	$+384a^3cd^2e^2$	$-46a^3b^2d^2f^2$	$+4080a^3bd^2e^2f$
$-2384a^2bd^2e$	$-216a^3d^4e$	$+117a^3b^2de^2f$	$-1920a^3bde^4$
$+128a^2c^2df$	$-4a^3b^2df^2$	$+18a^3b^2e^4$	$-1440a^3c^2ef^2$
$-1232a^2c^2e^2$	$-32a^3b^2e^2f$	$-168a^3bc^2df^2$	$+2640a^3c^2d^2f^2$
$+4896a^2c^2d^2e$	$-81a^3b^2c^2f^2$	$+276a^3bc^2e^2f$	$+4480a^3c^2de^2f$
$-1632a^2cd^4$	$+348a^3b^2cdef$	$-220a^3bcd^2ef$	$-2560a^3c^2e^4$
$+49a^2b^4f^2$	$+200a^3b^2ce^3$	$-504a^3bde^3$	$-10080a^3cd^3ef$
$+180a^2b^3cef$	$+28a^3b^2d^3f$	$+144a^3bd^4f$	$+5760a^3cd^2e^2$
$+224a^2b^3d^2f$	$+275a^3b^2d^2e^2$	$+276a^3bd^3e^2$	$+3456a^3d^3f$
$+460a^2b^3de^2$	$+116a^3bc^2ef$	$+108a^3c^2f^2$	$-2160a^3d^4e^2$
$+344a^2b^2c^2df$	$-336a^3bc^2d^2f$	$-264a^3c^2def$	$-640ab^3cf^2$
$+3880a^2b^2c^2e^2$	$-780a^3bc^2de^2$	$-448a^3c^2e^3$	$+320ab^3def^2$
$+3000a^2b^2cd^2e$	$-960a^3bcd^2e$	$+96a^3c^2d^2f$	$-180ab^3e^2f$
$+6400a^2b^2d^4$	$+864a^3bd^4$	$+1736a^3c^2d^2e^2$	$+4080ab^2c^2ef^2$
$-384a^2bc^3f$	$+64a^3c^4df$	$-1584a^3cd^4e$	$+4480ab^2cd^2f^2$
$-20160a^2bc^2de$	$-60a^3c^4e^2$	$+432a^3d^6$	$-14920ab^2cde^2f$
$+8480a^2c^4e$	$+1120a^3c^3d^2e$	$-12ab^1ef^2$	$+7200ab^2ce^4$
$-1120a^2c^4d^2$	$-720a^3c^3d^3$	$+264ab^3cdf^2$	$+960ab^2d^3ef$
$-170ab^4ef$	$+84ab^4ef^2$	$-615ab^3ce^2f$	$-600ab^2d^3e^2$
$-860ab^4cdf$	$-100ab^4def$	$-12ab^3d^2ef$	$-10080abc^2df^2$
$-4450ab^4ce^2$	$-60ab^4e^3$	$+45ab^3de^3$	$+960abc^2e^2f$
$-2700ab^4d^2e$	$-310ab^3c^2ef$	$-180ab^3c^2f^2$	$+28480abc^2d^2ef$
$+23400ab^3c^2de$	$-100ab^3cd^2f$	$+1188ab^3c^2def$	$-16000abc^2de^3$
$+680ab^3c^3f$	$-890ab^3cde^2$	$+1410ab^3c^2e^3$	$-11520abcd^4f$
$-29600ab^3cd^3$	$-140ab^3d^3e$	$-616ab^3cd^2f$	$+7200abcd^3e^2$
$-11200ab^3c^4e$	$+520ab^3c^2df$	$-1140ab^3cd^2e^2$	$+3456ac^4f^2$
$+44800ab^2c^3d^2$	$+1120ab^3c^2e^2$	$+120ab^3d^4e$	$-11520ac^4def$
$-27200abc^4d$	$+4920ab^2c^2d^2e$	$-288abc^4ef$	$+6400ac^4e^3$
$+6400ac^7$	$-3120ab^2cd^4$	$+192abc^3d^2f$	$+5120ac^3d^4f$
$+400b^5df$	$-192abc^5f$	$-3720abc^3de^2$	$-3200ac^3d^2e^2$
$+1625b^5e^2$	$-6560abc^5de$	$+4640abc^3d^3e$	$+256b^7f^3$
$-300b^5c^2f$	$+4160abc^3d^3$	$-1440abcd^5$	$-1920b^6cef^2$
$-7500b^5cde$	$+1920ac^6e$	$+1440ac^4e^3$	$-2560b^6d^2f^2$
$+14000b^5d^3$	$-1280ac^4d^2$	$-1920ac^4d^2e$	$+7200b^6de^2f$
$+4000b^5c^2e$	$-28b^6f^2$	$+640ac^3d^4$	$-3375b^6e^4$
$-24000b^5cd^2$	$+140b^6cef$	$-96b^6df^2$	$+5760b^5c^2df^2$
$+16000b^5c^4d$	$+120b^6d^2f$	$+270b^6e^2f$	$-600b^5c^2e^2f$
$-4000b^5c^6$	$+600b^6de^2$	$+72b^6c^2f^2$	$-16000b^5cd^2ef$
	$-320b^5c^2df$	$-600b^6cdef$	$+9000b^5cde^3$
	$-625b^5c^2e^2$	$-675b^6ce^3$	$+6400b^5d^4f$
	$-2700b^5cd^2e$	$+320b^5d^3f$	$-4000b^5d^3e^2$
	$+1700b^5d^4$	$+450b^5d^2e^2$	$-2160b^5c^4f^2$
	$+120b^5c^4f$	$+180b^5c^2ef$	$+7200b^5c^3def$
	$+3800b^5c^3de$	$-120b^5c^4f^2$	$-4000b^5c^3e^3$
	$-2400b^5c^3d^3$	$+2100b^5c^3de^2$	$-3200b^5c^3d^2f$
	$-1200b^5c^5e$	$-2600b^5cd^3e$	$+2000b^5c^3d^4e^2$
	$+800b^5c^4d^2$	$+800b^5d^5$	
		$-900b^5c^4e^2$	
		$+1200b^5c^3d^2e$	
		$-400b^5c^5d^4$	

The coefficients in the preceding equations of differences are functions of the seminvariants of the quantics to which they belong; for instance, in the case of the quartic, the coefficient of θ^4 is

$$8a^3\{a^2(ae-4bd+3c^2)+96(ac-b^2)^2\},$$

that of θ^3 is

$$32\{-13a^2(ace-ad^2-b^2e+2bcd-c^3)+16a^2(ac-b^2)(ae-4bd+3c^2)+128(ac-b^2)^3\},$$

and so for the other coefficients; and by replacing each seminvariant by the covariant to which it belongs, we pass from the solution of the original problem of finding the equation for $\theta=(\alpha-\beta)^2$, to that of the problem of finding the equation for

$$\theta=\frac{(\alpha-\beta)^2}{(x-\alpha y)^2(x-\beta y)^2}.$$

The results are as follows:—

For the quadric $(a, b, c)(x, y)^2$, the equation in θ is, $0=$

$$(U^2,\ 4\square)(\theta, 1)^2,$$

where U is the quadric, $\square$ the discriminant.

For the cubic $(a, b, c, d)(x, y)^3$, the equation in θ is, $0=$

$$(U^4,\ 18U^2H,\ 81H^2,\ 27\square)(\theta, 1)^3,$$

where U is the cubic, H the Hessian, $\square$ the discriminant.

For the quartic $(a, b, c, d, e)(x, y)^4$, the equation in θ is, $0=$

$$\left\{\begin{array}{l} U^6, \\ 48U^4H, \\ 8U^2(U^3I+96H^2), \\ 32(-13U^3J+16U^2HI+128H^3), \\ 16(-\ 7U^3I^2-288UHJ+384H^2I), \\ 1152(-3UIJ+2HI^2), \\ 256(\ \ I^3\ -27J^2), \end{array}\right\}(\theta, 1)^6,$$

where U is the quartic, H the Hessian, I and J the quadrinvariant and the cubinvariant respectively.

For the quintic $(a, b, c, d, e, f)(x, y)^5$, the equation in θ, as far as it can be expressed in terms of known covariants, is, $0=$

$$\left\{\begin{array}{l} U^8, \\ 100U^6(\text{Tab. No. 15}), \\ 50U^4[U^2(\text{Tab. No. 14})+75(\text{Tab. No. 15})^2], \\ . \\ . \\ . \\ 3125\ \text{Discriminant}(=\text{Tab. No. 26}) \end{array}\right\}(\theta, 1)^{10},$$

where the Tables referred to are those in my Second Memoir on Quantics.

The form of the preceding results may be modified by writing $\theta = \mathfrak{S} \div U^2$; we have thus the equations for

$$\mathfrak{S} = a^2(\alpha-\beta)^2(x-\gamma y)^2(x-\delta y)^2\ldots;$$

thus for example, in the case of the cubic $(a, b, c, d)(x, y)^3$, the equation for $\mathfrak{S}[=a^2(\alpha-\beta)^2(x-\gamma y)^2]$ is

$$0 = (1,\ 18H,\ 81H^2,\ 27\square U^2)(\mathfrak{S}, 1)^3.$$

This equation may be written

$$(\mathfrak{S}+9H)^2\mathfrak{S}+27\square U^2 = 0;$$

or putting $v = \sqrt{\mathfrak{S}}$, we have

$$v^3+9Hv+U\sqrt{-27\square} = 0,$$

an equation the roots of which are

$$a(\alpha-\beta)(x-\gamma y),\quad a(\beta-\gamma)(x-\alpha y),\quad a(\gamma-\alpha)(x-\beta y),$$

and which leads to the formula, given in my Fifth Memoir on Quantics, for the solution of a cubic equation. But this decomposition of the equation in $\mathfrak{S}$ is peculiar to the cubic.

The equation of differences for an equation of any order may be found by the following entirely distinct method. Let the proposed equation $(*)(v, 1)^n = 0$, be for shortness represented by $\varphi v = 0$, and let x, y be any two distinct roots; we have not only

$\varphi x = 0$, $\varphi y = 0$, but also $\varphi x + \varphi y = 0$, $\frac{\varphi x - \varphi y}{x-y} = 0$. Writing $\theta = (x-y)^2$, $s = x+y$, we have

$$x = \tfrac{1}{2}(s+\sqrt{\theta}),\quad y = \tfrac{1}{2}(s-\sqrt{\theta}),$$

values which are to be substituted for x, y in the equations

$$\varphi x + \varphi y = 0,\quad \frac{\varphi x - \varphi y}{x-y} = 0.$$

We have thus two equations rational in s and θ, and the elimination between them of the quantity s leads to the required equation in θ. But it is proper to modify the form of the system; in fact the two equations are, as regards s, the first of them of the degree n, the second of the degree $n-1$; but if we write

$$n(\varphi x + \varphi y) - \frac{(x+y)(\varphi x - \varphi y)}{x-y} = 0,\quad \frac{\varphi x - \varphi y}{x-y} = 0,$$

then each of the equations will be of the same degree $n-1$ in s.

For instance, let $\varphi v = (a, b, c, d)(v, 1)^3$, then $x = \frac{1}{2}(s+\sqrt{\theta})$, $y = \frac{1}{2}(s+\sqrt{\theta})$; the equations $\varphi x + \varphi y = 0$, $\frac{\varphi x - \varphi y}{x-y} = 0$, are

$$\begin{aligned} s^3a + 3s^2 2b + 3s(4c + a\theta) + 8d + 6b\theta &= 0,\\ 3s^2a + 3s\ 4b + \ 12c + a\theta &= 0; \end{aligned}$$

and multiplying the first equation by 3 and the second by $-s$, adding and dividing by 2, we have an equation

$$s^3 3b + s(12c + 4a\theta) + 12d + 9b\theta = 0.$$

The second equation and this equation may be written

$$(3a,\ 12b\quad 12c+a\theta\ \Big|\ s,\ 1)^3=0,$$
$$(3b,\ 12c+4a\theta,\ 12d+9b\theta\ \Big|\ s,\ 1)^3=0,$$

and the elimination of s from these equations gives the required equation in θ. The result may be obtained under either of the two forms,

$$\{a^2\theta^2+(15ac-27b^2)\theta-36(bd-c^2)\}\{a^2\theta+3\ (ac-b^2)\}+3\{2ab\theta+3(ad-bc)\}^2=0$$

and

$$\{4a^3\theta^2+(24ac-27b^2)\theta-36(bd-c^2)\}\{a^2\theta+12(ac-b^2)\}+3\{\ ab\theta+6(ad-bc)\}^2=0,$$

the expansions of which respectively coincide with the before-mentioned result.

In the case of the quartic equation $\varphi v=(a,\ b,\ c,\ d\ \Big|\ v,\ 1)^4=0$, we have

$$s^4a+4s^32b+6s^2(\ 4c+a\theta)+4s(8d+6b\theta)+16e+24c\theta+a\theta^2=0,$$
$$4s^3a+6s^24b+4s\,(12c+a\theta)+\ 32d+8b\theta\qquad\qquad=0,$$

from which we derive another cubic equation; and the two cubic equations are

$$(4a,\ \ 24b\quad ,\ \ 48c+\ 4a\theta,\ \ 32d+\ 8b\theta\quad\Big|\ s,\ 1)^3=0,$$
$$(4b,\ \ 24c+10a\theta,\ \ 48d+44b\theta,\ \ 32e+48c\theta+2a\theta^2\ \Big|\ s,\ 1)^3=0,$$

from which, if s be eliminated, we have the equation in θ.

Similarly, for the quintic equation $\varphi v=(a,\ b,\ c,\ d,\ e,\ f\ \Big|\ v,\ 1)^5=0$, we have

$$s^5a+\ 5s^42b+10s^3(\ 4c+a\theta)+10s^2(\ 8d+6b\theta)+5s(16e+24c\theta+a\theta^2)+32f+80d\theta+10b\theta^2=0,$$
$$5s^4a+10s^34b+10s^2(12c+a\theta)+\ 5s\,(32d+8b\theta)+\ \ (80e+40c\theta+a\theta^2)\qquad\qquad=0,$$

from which we derive another quartic equation; the two equations are

$$(5a,\ \ 40b\quad ,\ \ 120c+\ 10a\theta,\ \ 160d+\ 40b\theta\quad ,\ \ 80e+\ 40c\theta+\ \ a\theta^2\ \Big|\ s,\ 1)^4=0,$$
$$(5b,\ \ 40c+20a\theta,\ \ 120d+130b\theta,\ \ 160e+280c\theta+12a\theta^2,\ \ 80f+200d\theta+25b\theta^2\ \Big|\ s,\ 1)^4=0,$$

from which, if s be eliminated, we have the equation in θ.

But to apply Bezout's method to the two equations each of the order $n-1$, which result from the equation of the nth order $\varphi v=(*\ \Big|\ v,\ 1)^n=0$. The process is as follows:— Suppose, in general, that s is to be eliminated from the two equations

$$Fs=0,\quad Gs=0,$$

each of the order $n-1$; it is only necessary to form the expression

$$\frac{FsG's'-Fs'Gs}{s-s'},$$

which will be a function of s, s' of the form

$$\begin{pmatrix} a_{0,0},\ a_{0,1}\ \ldots\ a_{0,n-2}\ \Big|\ s,\ 1)^{n-2}(s',\ 1)^{n-2} \\ a_{1,0}, \\ \vdots \\ a_{n-2,0} \end{pmatrix}$$

where the coefficients are such that $a_{i,m}=a_{m,i}$; and by equating to zero the determinant formed with these coefficients, we have the result of the elimination.

In the present case, writing for a moment $\phi\frac{1}{2}(s+\sqrt{\theta})=A$, $\phi\frac{1}{2}(s-\sqrt{\theta})=B$, and in like manner $\phi\frac{1}{2}(s'+\sqrt{\theta})=A'$, $\phi\frac{1}{2}(s'=\sqrt{\theta})=B'$, we have

$$Fs=n(A+B)-\frac{s(A-B)}{\sqrt{\theta}}, \quad Gs=\frac{A-B}{\sqrt{\theta}},$$

$$Fs'=n(A'+B')-\frac{s'(A'-B')}{\sqrt{\theta}}, \quad Gs'=\frac{A'-B'}{\sqrt{\theta}},$$

and therefore

$$FsGs'-Fs'Gs=n\frac{(A+B)(A'-B')-(A-B)(A'+B')}{\sqrt{\theta}}-\frac{(s-s')(A-B)(A'-B')}{\theta};$$

or reducing and dividing by $s-s'$,

$$-\frac{FsGs'-Fs'Gs}{s-s'}=2n\frac{AB'-A'B}{\sqrt{\theta}(s-s')}+\frac{(A-B)A'-B'}{\theta}.$$

Hence, substituting for A, B, A′, B′ these values, we have the expression

$$2n\frac{\phi\frac{1}{2}(s+\sqrt{\theta})\phi\frac{1}{2}(s'-\sqrt{\theta})-\phi\frac{1}{2}(s-\sqrt{\theta})\phi\frac{1}{2}(s'+\sqrt{\theta})}{(s-s')\sqrt{\theta}}$$
$$+\frac{\{\phi\frac{1}{2}(s+\sqrt{\theta})-\phi\frac{1}{2}(s-\sqrt{\theta})\}\{\phi\frac{1}{2}(s'+\sqrt{\theta})-\phi\frac{1}{2}(s'-\sqrt{\theta})\}}{\theta},$$

which is of the form

$$\begin{vmatrix} a_{0,0}, & a_{0,1} & \ldots & a_{0,n-2} \\ a_{1,0} & & & \\ \cdot & & & \\ \cdot & & & \\ a_{n-2,0} & & & \end{vmatrix} (s,1)^{n-2}(s,1)^{n-2}$$

and equating to zero the determinant formed with the coefficients, we have an equation in θ which is the equation of differences of the given equation $\phi v=0$. For instance, if the given equation is $\phi v=(a, b, c, d)(v, 1)^3=0$, then we have

$$8\phi\tfrac{1}{2}(s+\sqrt{\theta})=(a, 2b+a\sqrt{\theta}, 4c+4b\sqrt{\theta}+a\theta, 8d+12c\sqrt{\theta}+6b\theta+a\theta\sqrt{\theta})(s, 1)^3$$
$$=(A, B, C, D)(s, 1)^3,$$

$$8\phi\tfrac{1}{2}(s-\sqrt{\theta})=(a, 2b-a\sqrt{\theta}, 4c-4b\sqrt{\theta}+a\theta, 8d-12c\sqrt{\theta}+6b\theta-a\theta\sqrt{\theta})(s, 1)^3$$
$$=(A', B', C', D')(s, 1)^3;$$

and the function in s, s' is

$$\frac{6}{\sqrt{\theta}}\left\{\begin{array}{l} 3(AB'-A'B)s^2s'^2 \\ +3(AC'-A'C)ss'(s+s') \\ +(AD'-A'D)(s^2+ss'+s'^2) \\ +9(BC'-B'C)ss' \\ +3(BD'-B'D)(s+s') \\ +3(CD'-C'D) \end{array}\right\}$$
$$+\tfrac{1}{\theta}(A-A', B-B', C-C', D-D')(s, 1)^3(A-A', B-B', C-C', D-D')(s', 1)^3,$$

which is equal to

$$12\left\{\begin{array}{l} -3a^2\,s^2s'^2 \\ -12ab\;ss'(s+s') \\ +(-12ac-a^2\theta)(s^2+ss'+s'^2) \\ +(36ac-72b^2+9a^2\theta)ss' \\ +(24ad-72bc+12ab\theta)(s+s') \\ +96bd-144c^2+(-48ac+72b^2)\theta-3a^2\theta^2 \end{array}\right\}$$
$$+4(3as^2+12bs+12c+a\theta)(3as'^2+12bs'+12c+a\theta);$$

or reducing and dividing by 32, this is

$$\{9(ac-b^2)+3a^2\theta\}ss'$$
$$+\{9(ad-bc)+6ab\theta\}(s+s')$$
$$+36(bd-c^2)+(-15ac+27b^2)\theta-a^2\theta^2,$$

the terms in s^2, s'^2 disappearing, as they should do. Writing this under the form

$$\left|\begin{array}{ll} 9(ac-b^2)+3a^2\theta, & 9(ad-bc)+6ab\theta \\ 9(ad-bc)+6ab\theta, & 36(bd-c^2)+(-15ac+27b^2)\theta-a^2\theta^2 \end{array}\right|(s,1)(s',1)$$

and equating the determinant to zero, we have the required equation in θ: the form is precisely that which is obtained by the ordinary process of applying Bezout's method to the two equations

$$(3a,\ 12b,\ \ 12c+\ a\theta)(s,1)^2=0,$$
$$(3b,\ 12c+4a\theta,\ 12d+8b\theta)(s,1)^2=0,$$

being in fact the before-mentioned equation

$$\big(a^2\theta^2+(15ac-27b^2)\theta-36(bd-c^2)\big)\big(a^2\theta+3(ac-b^2)\big)+3\big(2ab\theta+3(ad-bc)\big)^2=0.$$

But, as already remarked, this elimination process is less convenient for the complete development of the result, than the method first explained in the present memoir.

VII. *On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and other Gases.* *By* THOMAS ANDREWS, *M.D., F.R.S., M.R.I.A., Vice-President of Queen's College, Belfast; and* PETER G. TAIT, *M.A., late Fellow of St. Peter's College, Cambridge, Professor of Mathematics in Queen's College, Belfast.*

Received February 20,—Read March 29, 1860.

§ 1.

THE molecular changes produced by the electric current, or discharge, in certain compound bodies through which it is transmitted, furnish some of the most interesting examples of the action of a decomposing force that have been discovered in later times. The discharge of the Leyden jar, through fine wires or thin metallic leaves, exhibited long ago the heating power of the current, and the interesting experiments of the Dutch chemists afterwards showed that the disruptive discharge has the power of splitting up compound bodies into their constituent parts. The great invention of the pile of VOLTA, by furnishing an abundant supply of electricity of moderate tension, led subsequently to the important discovery of the polar decomposition of water and of other compound bodies. In the case of gases, it has been known, since the time of PRIESTLEY and CAVENDISH, that the spark discharge has the apparently antagonistic properties of causing decomposition in some cases and combination in others. Finally, in our own day, SCHÖNBEIN made the fine observation that a new substance (ozone), alike remarkable for the activity of its properties and for the facility with which it is destroyed, is formed by the action of the spark on pure oxygen gas, in the electrolysis of water, and in certain cases of slow oxidation.

Our object in the present communication is to continue the investigation, already begun by one of us*, of the properties of ozone, by subjecting it under varied conditions to a series of careful volumetric experiments. We hoped, in this way, to throw some new light on the relations of this singular body to oxygen, by determining whether any, and what, change of volume occurs in its formation. Our expectations in this respect have not been disappointed. We have ascertained that when oxygen changes into ozone, a great condensation takes place; so great indeed, that it is almost incompatible with the existence of ozone as an allotropic form of oxygen in the gaseous state. This investigation has naturally extended itself to an examination of the effects produced by the electrical discharge upon other gases, simple as well as compound; and although, from its great extent, this part of the inquiry has as yet been only partially entered into,

* Philosophical Transactions, 1856, p. 1.

some of the results already obtained are of considerable interest, and will be referred to in the present communication.

Before proceeding further, we must draw attention to the difference of action which, in many cases, we have found to exist between the spark, or spark discharge, and the glow, or silent discharge. When the former terms are employed in this paper, they indicate a succession of brilliant sparks between two fine platinum wires, usually at the distance of 20 millims. (0·8 inch) from each other, and hermetically sealed into the tube containing the gas under observation. This form of discharge was obtained by connecting the free end of one of the platinum wires with an insulating stand, provided with a brass ball which was brought within a short distance of the prime conductor of an electrical machine in high order, while the free end of the other platinum wire was in connexion with the ground. The silent discharge presented no visible character except a faint glow, not visible by daylight, at each metallic point, and was obtained by connecting the first platinum wire, not with the insulator, but directly with the prime conductor. To avoid the mixture of the "brush" with the silent discharge, it was necessary to establish the connexion firmly both with the conductor and with the earth wire; and, in some cases, where a full effect was required, the machine had to be turned very slowly.

The electrical machine employed was a small plate one (18 inches in diameter), screwed down firmly to the floor of the apartment, opposite to an open fire. On the prolongation of the axis of the plate, a wheel, 6 inches in diameter, was fixed, from which a belt passed to an iron wheel, 40 inches in diameter, revolving in a wooden frame, which was also fastened to the floor. By this arrangement, the machine could be easily made to turn at the rate of 350 revolutions per minute. To maintain a regular and powerful stream of electricity at this rapid rate of motion, it was found necessary, in addition to the ordinary cushions, to hold with the hand against the plate a rubber covered with amalgam. When in ordinary working order, the machine gave above 600 sparks per minute, and in decomposing water produced in the same time 0·0002 cub. cent. of the mixed gases*.

The ordinary forms of eudiometrical apparatus were found to be wholly inapplicable to this inquiry. We failed in discovering, by their means, whether even a change of volume occurs, when ozone is produced from oxygen. To increase the difficulty, the experiments could not be carried on in presence of mercury or water, as the former is immediately attacked by ozone; and the latter not only destroys it rapidly by contact, but introduces a disturbing cause, in the form of aqueous vapour, exceeding in general the whole effect to be measured. In the apparatus now to be described these difficulties were overcome, and very minute changes of volume determined with certainty.

In Plate III. figs. 1 and 2, the vessel in which the oxygen was contained is represented of different forms. It consists of a cylindrical tube *ab*, having two fine platinum wires hermetically sealed in opposite sides, and terminating in a capillary tube *cde*, of the

* Reports of the British Association for 1855, Trans. of Sect. p. 46.

form represented in the figure. The liquid in the limbs *d*, *e* is hydrated sulphuric acid (HO, SO_3), and it is by the changes in the level of this liquid that the alteration in the volume of the gas in *abc* is determined. In order to make the necessary corrections for changes of temperature and pressure, during the interval between two observations, a vessel filled with dry air, of the same form and size as that employed in the experiment, was read along with it; the reservoirs of both vessels being immersed in a large calorimeter, as shown in fig. 3. To the first of these vessels, we usually gave the name of *primary* vessel, and to the second that of *auxiliary* vessel. In order to correct for any slight difference in the size of the vessels, or in the diameters of the capillary tubes, simultaneous readings of both were made at different temperatures, and a coefficient thus determined, by means of which the indications of the two vessels could be afterwards accurately compared. When the reservoirs were large, the corrections so to be applied were frequently less than the errors of observation.

The extreme delicacy of this apparatus will be evident from the following considerations. If we take the case of a vessel with a large reservoir (fig. 1), the changes in volume of the contained gas, supposing the temperature to remain constant, will be nearly proportional to the changes of pressure indicated by a barometer filled with sulphuric acid. As the height of such a barometer, at the mean pressure of the atmosphere, would be about 5500 millims., an alteration of 1 millim. in the difference of levels of the acid in the siphon tube (*de*, fig. 1) would correspond to a change of volume of about $\frac{1}{5000}$th of the entire gas; but, as it was easy to read to 0·5 millim., or even to 0·25 millim., the apparatus in this form enabled us to estimate a change of volume not exceeding one-half, or even one-fourth of that quantity. With a smaller reservoir (fig. 2), the indications of the apparatus were, it is true, not quite so delicate, and a careful set of comparative readings with the auxiliary vessel was always required; but even here, a change of volume, amounting to not more than $\frac{1}{5000}$th of the whole, could be determined with certainty.

The absolute change of volume of the gas, corresponding to a given change in the levels of the acid in the siphon tube (corrected in the first instance by the aid of the auxiliary vessel), was estimated in two ways; first, by observing the change of level produced by raising or lowering the temperature of the water in the calorimeter through a small number of degrees; and secondly, by accurately determining, at the end of the experiment, the capacity of the reservoir and that of the capillary tube.

The form of apparatus now described can only be employed when the entire change of volume of the gas does not amount, in the course of the experiment, to more than about one-tenth of the whole. When large changes of volume occur, the free end of the siphon tube must be hermetically sealed, so as to include a certain quantity of air, from whose subsequent change of volume that of the gas in the reservoir can be readily calculated. This modification of the apparatus we have found to be very convenient in experiments upon the action of the spark and silent discharge on the compound gases.

§ 2.

The oxygen gas employed in the following experiments was prepared from fused chlorate of potash, and, to purify and dry it, was passed through two U-tubes; the first containing fragments of marble moistened with a strong solution of caustic potash, the second, fragments of glass moistened with sulphuric acid. The potash tube was sometimes suppressed. In order to remove every trace of nitrogen, the whole apparatus was placed in connexion with a good air-pump, and a vacuum produced to the extent of at least half an inch, while the gas was still being evolved from the fused chlorate (fig. 4). When the process of exhaustion was discontinued, the gas soon filled the apparatus, and was expelled through the mercury at the lower end of the long gauge. The operation of exhausting and refilling the vessel was performed three times in every experiment. Supposing the connexions of the apparatus to have been perfectly air-tight, the nitrogen remaining, after this triple exhaustion, could not have amounted to more than $\frac{1}{200,000}$th of the whole. This degree of accuracy was not, it is true, realized in practice, but the oxygen gas, prepared in this way, did not contain $\frac{1}{1000}$th of its volume of nitrogen. The connexion with the air-pump at a having been broken (the gas still continuing to pass freely over), the end of the tube was softened in a lamp and bent downwards at an obtuse angle, so as to allow it to dip into sulphuric acid contained in a small dish, as shown in fig. 5. The current of gas was now arrested, by removing gradually the lamps from the chlorate of potash, so as to allow the apparatus to cool slowly. When the acid had ascended a short way in $a\,c$, the vessel was sealed hermetically at b, and, after the acid had ascended to about the point c, the vessel was removed, and placed in the upright position represented in figs. 1 and 2. It was sometimes necessary to expel a bubble or two of gas, in order that the column of acid in the siphon tube might be in a convenient position when the vessel was placed in the calorimeter.

Previous to filling the vessels, they were always cleaned by means of boiling nitric acid, and subsequent washing with distilled water. They were afterwards carefully dried. To the success of several of the following experiments, this precaution was indispensable.

An auxiliary vessel having been filled in the same manner, either with air or with oxygen, the two vessels were placed in the calorimeter (fig. 3), and the difference of the levels of the acid in each carefully read. In our earlier experiments we generally used a cathetometer for this purpose, but latterly we found it more convenient and sufficiently accurate to apply to the limbs of the siphon tubes a scale divided into millimetres. From the rapidity indeed with which the readings were thus made, the results were found to be fully as trustworthy as those obtained with the cathetometer. When quantitative determinations were required, the temperature of the water in the calorimeter and the height of the barometer were carefully noted.

After the levels were read, the free ends of the siphon tubes in both vessels were hermetically sealed. The primary vessel was then removed from the calorimeter and placed in connexion with the electrical machine, to be exposed to the action either of

the spark or silent discharge. When this operation was finished, the vessel was replaced in the calorimeter, the siphon tubes were opened, and the levels of the acid in the two vessels again read.

In order to examine the effects of heat, the reservoir of the vessel was placed in a sort of air-bath, formed by suspending a long copper cylinder above a LESLIE'S gas-burner, the siphon tube being outside the cylinder, fig. 6. In this way a temperature of 300° C., which was sufficient to destroy in a short time all the ozone reactions, was readily obtained. This temperature was estimated without difficulty, by observing the amount of compression of the air in the outer leg of the siphon tube. Our apparatus, with a slight modification, might, in fact, be employed as a thermometer for all temperatures below that at which glass begins to soften.

It will probably tend to perspicuity, if we state, before going further, some of the general results of our experiments on the action of the electrical discharge on pure oxygen.

I. *When the silent discharge is passed through pure and dry oxygen, a contraction takes place. This contraction proceeds, at first rapidly, but afterwards more slowly, till it attains a limit, which, in one of our experiments, amounted to* $\frac{1}{12}$*th of the original volume of the gas.*

II. *If a few electrical sparks be passed through the gas in this contracted state, it expands till it recovers about three-fourths of the contraction; but, however long the sparks are passed, the gas never recovers its original volume.*

III. *When electrical sparks are passed through pure and dry oxygen, it contracts, but to a much smaller extent than when acted on by the silent discharge. The oxygen is, in fact, brought to the same volume as when electrical sparks are passed through the same gas, previously contracted by the silent discharge.*

IV. *When oxygen, contracted either by the silent discharge or by sparks, is exposed for a short time to the temperature of* 270° *C., it is restored to its original volume, and, on opening the vessel, the ozone reactions are found to have disappeared.*

The following experiments, taken from a large number which gave similar results, will serve to illustrate the foregoing statements.

α. In a vessel, whose reservoir had a capacity of 5 cub. cent., sparks were passed for ten minutes, and produced a contraction of 5·9 millims., as measured by the change of levels of the acid in the siphon tube. By heating the vessel afterwards to 300° C., the levels were restored to within 0·1 millim. of their original position.

With the silent discharge in the same vessel, a contraction of 39·5 millims. (corresponding to about one-thirtieth of the volume of the gas) was obtained in ten minutes. Of this contraction heat restored 38·7 millims. This slight difference of 0·8 millim. is probably due to distortion of the vessel produced by heat.

Again, the silent discharge gave in ten minutes a contraction of 37·6 millims., of which sparks, subsequently passed for seven minutes, destroyed 29·7 millims., leaving 7·9 millims. undestroyed.

β. In another vessel, having a reservoir of the capacity of 0·8 cub. cent., active sparks gave, in fifteen minutes, 4 millims. of contraction. After fifteen minutes more of sparks there was no additional contraction.

The silent discharge was now passed for fifteen minutes, and increased the contraction to 20 millims.; in fifteen minutes more, the entire contraction was 31 millims. Four strong sparks reduced this to 22·5 millims., six or seven more to 16 millims., seven more to 11 millims., and sparks, continued for ten minutes, left 4 millims. of permanent contraction.

γ. In a third vessel, of about the same capacity as the last, sparks gave a final contraction of 7·5 millims.; while the silent discharge, pushed to its limit, increased the contraction to 90 millims., corresponding to about one-twelfth of the entire volume of the gas. This contraction was almost exactly destroyed by heat.

Before leaving this part of the subject, we should mention that, when a full contraction is obtained by means of the silent discharge, it will be found very slowly to diminish from day to day. We have not ascertained whether, at the end of a very long period of time, the original volume of the gas would be recovered. At 100° C., the contraction diminishes much more rapidly than at ordinary temperatures. Thus it appears that the state produced by the electrical discharge is not permanent, even at common temperatures, and that it becomes more unstable as the temperature rises, till at 270° C. it is rapidly destroyed.

§ 3.

We next proceeded to examine the volumetric changes which occur when oxygen, contracted by the electrical discharge, is brought into contact with other bodies.

The first body we tried was *mercury*, the physical changes produced on which by ozone are known to be very remarkable. When a capsule containing this metal is broken in a tube of oxygen gas through which the silent discharge has been passed, the mercury instantly loses its mobility, and, if gently shaken, covers the interior of the tube with a brilliant mirror. As the action continues, the mirrored surface breaks up, and the coating becomes converted into a blackish semipulverulent substance. Unless the tube be very violently shaken, the ozone reactions will not be entirely destroyed, until the mercury has been for some hours in contact with the gas.

To determine the volumetric changes, a thin capsule, filled with pure mercury and hermetically sealed, was placed in a vessel with a large reservoir of the usual form (fig. 1′), which was afterwards filled with dry oxygen. After the levels had been read, the silent discharge was passed until a considerable contraction was obtained. The corrections for changes of temperature and pressure were, as in other cases, furnished by an auxiliary vessel. The free end of the siphon tube having been sealed, the primary vessel was removed from the calorimeter, and the capsule broken by a sudden jerk. The breaking of the capsule, in this and other experiments, was greatly facilitated by introducing into the vessel a small piece of thick glass tube, which fell on the capsule when the vessel was shaken (fig. 1′, *k*).

Viewing ozone as an allotropic form of oxygen, in the gaseous state, we expected that when mercury came into contact with it, a contraction would take place, equal to the volume of the ozone which entered into combination with the metal. This anticipation has not been realized. After the rupture of the capsule, the vessel was immediately replaced in the calorimeter and the levels read. Not the slightest diminution of volume was observed in any one of a large number of experiments; on the contrary, an increase, corresponding to a change of 1 millim. in the levels, generally occurred. On allowing the vessels to remain in the calorimeter, and reading the position of the acid in the siphon tubes from time to time, the gas was found to expand steadily, but slowly, for some hours, till from two-thirds to five-sixths of the contraction produced by the discharge was recovered. If the vessel was opened at any time while this expansion was going on, the ozone reactions were always manifest; but, when the expansion was at an end, the ozone reactions had also ceased.

If the mercury, instead of being allowed tranquilly to act upon the gas, was violently agitated after breaking the capsule, a much smaller portion of the contraction was restored; in some cases not more than one-sixth.

Metallic *silver*, in the state both of leaf and of filings, gave similar results. The surface of the silver was partially blackened, about three-fourths of the original contraction was recovered, and the whole operation much more quickly terminated.

As the above reactions were evidently complex, the mercury and silver partly entering into combination with the gas, while the compounds formed appeared to exercise a catalytic action, we endeavoured to find an elementary body which would instantly destroy the ozone reactions, and at the same time be without action on dry oxygen. After some trials, we found that *iodine* possessed the required properties. We first ascertained that its vapour, although visible at common temperatures, has no appreciable tension. When a small capsule, containing pure and dry iodine, was broken in a vessel of the usual form filled with oxygen, the levels of the acid in the siphon tube were not altered. So slight also is the affinity of iodine for oxygen, that, on heating the reservoir so as to volatilize a considerable portion of the iodine, and afterwards allowing it to cool, the volume of the gas underwent no change. On the other hand, if ozone be present, the iodine is immediately attacked, a greyish-yellow compound is formed, and all ozone reactions are instantly destroyed.

The experiment already described with mercury was now repeated, substituting iodine for that metal. On breaking the capsule, the levels of the acid scarcely changed 1-millim., although the original contraction amounted to 50 millims. No subsequent expansion took place, and, on opening the vessel, the ozone reactions had entirely disappeared.

On the allotropic hypothesis, these experiments, and particularly the last, lead to the conclusion that ozone must have a density at least fifty times as great as that of oxygen. This conclusion is indeed unavoidable from the experiments just described, unless it is assumed that, at the same moment that one portion of the ozone combines with the iodine, another portion changes back into oxygen, and that these quantities are so

related to one another, that the expansion due to the one is exactly equal to the contraction arising from the other. Such a supposition can, however, not be considered probable.

§ 4.

In order to subject this remarkable property of ozone to a further examination, two additional series of experiments were undertaken, to a description of which we now proceed.

In the first series, a primary and an auxiliary vessel with large reservoirs were filled with pure and dry oxygen, small capsules hermetically sealed, and containing portions of the same solution of iodide of potassium, having been previously placed in each. The silent discharge was passed through the primary vessel so as to produce a considerable contraction, amounting in different experiments to from 40 millims. to 80 millims. The levels of the acid in the siphon tubes of both vessels having been carefully read while the vessels were in the calorimeter, the ends were sealed, and the vessels shaken so as to break the capsules in both. In the primary vessel, the iodide of potassium solution became instantly coloured dark brown from the iodine set free, while that in the auxiliary vessel did not change. On replacing the vessels in the calorimeter, and opening the ends of the siphon tubes, the change in the levels indicated a considerable expansion in both. In the auxiliary vessel, this expansion was due to the tension of the vapour of the solution of iodide of potassium alone; in the primary vessel, the expansion ought to have been less than this, on account of the absorption of ozone, if the volume of that body were capable of measurement.

In the following Table, which contains the results of five very careful experiments made in this way, the first column gives the amount of contraction produced by the silent discharge in the primary vessel, previous to the breaking of the capsules; the second, the temperature; the third and fourth, the respective expansions in the primary and auxiliary vessels; and the fifth, the differences of the numbers in the third and fourth columns:—

	mm.	°	mm.	mm.	mm.
I.	81·5	11·0 C.	68·5	70·0	−1·5
II.	62·2	13·5 C.	79·5	80·0	−0·5
III.	72·2	8·7 C.	50·7	52·0	−1·3
IV.	63·5	12·2 C.	71·5	73·0	−1·5
V.	45·5	16·2 C.	87·0	89·2	−2·2

The capacity of the vessels employed in these experiments was about 30 cub. cent., and the primary and its auxiliary were found, in each experiment, by careful comparative observations, to work accurately together. The solution of iodide of potassium was purposely employed of different strengths in the several experiments. In I. it contained $\frac{1}{100}$th part of iodide of potassium; in II. $\frac{1}{300}$th; in III. $\frac{1}{3}$rd; and in IV. and V. $\frac{1}{8}$th. In the two last the solution was slightly acidulated with hydrochloric acid, in the others it was neutral. The capsules contained each about 0·7 grm. of these solutions.

The agreement in the results of these experiments, made with solutions of iodide of potassium so widely differing, is very remarkable. We ought also to observe that direct experiments, performed with great care, showed that the iodine set free by the ozone in the primary vessel did not affect the tension of the vapour of the solution.

Taking the mean of the above numbers, the density of ozone, as compared with that of oxygen, must be expressed, on the allotropic hypothesis, by about the number 60; in other words, ozone must be a gas only about six times lighter than the metal lithium. If the small differences in the fifth column be due, wholly or in part, to accidental causes, which is far from improbable, a still higher number must, on the same hypothesis, be taken to express the density of ozone.

In the last series of experiments, the amount of iodine set free in the solution of iodide of potassium was determined by analysis, and the weight of oxygen deduced therefrom compared with the weight of oxygen, calculated from the volumetric change which had occurred in the formation of the ozone.

We shall describe these experiments with some detail, particularly as the methods employed will be found applicable to other cases of gas analysis, where small changes in a given volume of gas have to be estimated.

Before filling it with oxygen, a sealed capsule containing a solution of iodide of potassium was introduced into the primary vessel, while the auxiliary contained the dry gas only. The silent discharge was passed through the former, and the contraction carefully observed. The capsule was then broken, and the solution agitated in the primary vessel for a few seconds. The siphon tube was next cut off, and the liquid carefully washed out and analysed by means of a weak solution of sulphurous acid, the exact strength of which had been immediately before determined by observing the amount required to decolorize a solution containing a known weight of iodine.

In some of the experiments the solution of iodide of potassium was slightly acidulated, in the others it was neutral. In the latter case it was acidulated before being analysed. The results were the same, whether the solution was taken in the neutral or in the acid state. For, although oxygen gas acts upon an acid solution of iodide of potassium, the action requires time, and the contact in this case was only continued for a few seconds*.

The formula by which we calculated the results of these experiments may be thus investigated.

Let f, g (fig. 1) be the mean level of the acid in the legs of the siphon tube; d, e the levels at any time, t being the temperature, and Π the barometric pressure corrected for

* Baumert has objected on this ground to some of the experiments in a former communication made by one of us to the Society. We have found that, in the circumstances in which those experiments were performed, about one-twentieth of the effect was due to this cause; but as the oxygen acting on the solution of iodide of potassium set free its equivalent of iodine, the equality of the numbers given in that paper could not be disturbed by this action. We have, since that time, by additional experiments, fully confirmed the statement that no water is produced in the destruction of electrolytic ozone by heat.

temperature. Let also $ge=fd=x$, and let H be the length of a tube similar to the siphon tube, and whose capacity is equal to that of the reservoir and of the siphon tube to f. Let a be the height of a barometer containing the liquid in the siphon tube, p the pressure of the gas in the vessel, and V the volume of the gas reduced to 0° C. and 760 millims.

Then, evidently,

$$p \propto V \frac{1+at}{H+x}.$$

But

$$p = \Pi\left(1+\frac{2x}{a}\right),$$

hence

$$\frac{V(1+at)}{\Pi(H+x)\left(1+\frac{2x}{a}\right)}$$

is a constant quantity. Taking the logarithmic differential, we have

$$0=\frac{\delta V}{V}+\frac{a\delta t}{1+at}-\frac{\delta\Pi}{\Pi}-\frac{\delta x}{H+x}-\frac{\frac{2\delta x}{a}-\frac{2x\delta a}{a^2}}{1+\frac{2x}{a}}.$$

Now $\frac{\delta a}{a}=\frac{\delta\Pi}{\Pi}$ is multiplied by $\frac{x}{a}$, a quantity rarely exceeding $\frac{1}{100}$. To this degree of approximation, then, at least,

$$\frac{\delta V}{V}+\frac{a\delta t}{1+at}-\frac{\delta\Pi}{\Pi}=\delta x\left(\frac{2}{a}+\frac{1}{H}\right). \quad \ldots\ldots\ldots \quad (1.)$$

If V_1, H_1, x_1 represent for the auxiliary vessel the quantities corresponding to V, H, x in the primary, we have, since $\delta V_1=0$,

$$\frac{a\delta t}{1+at}-\frac{\delta\Pi}{\Pi}=\delta x_1\left(\frac{2}{a}+\frac{1}{H_1}\right). \quad \ldots\ldots\ldots \quad (2.)$$

If $H_1=H$, *i. e.* if the primary and auxiliary vessels be of similar dimensions, we have at once, from (1.) and (2.),

$$\frac{\delta V}{V}=(\delta x-\delta x_1)\left(\frac{2}{a}+\frac{1}{H}\right). \quad \ldots\ldots\ldots \quad (3.)$$

If the vessels be not similar, let

$$\delta x_1\left(\frac{2}{a}+\frac{1}{H_1}\right)=\delta x_{11}\left(\frac{2}{a}+\frac{1}{H}\right),$$

then instead of (3.) we have

$$\frac{\delta V}{V}=(\delta x-\delta x_{11})\left(\frac{2}{a}+\frac{1}{H}\right). \quad \ldots\ldots\ldots \quad (4.)$$

Formula (3.) or (4.) gives the change of volume in the gas, as deduced from the observed change in the levels in the siphon tube.

For the estimation of the portion of the gas ($\delta_1 V$) taken up as ozone by the solution of iodide of potassium, let C be the capacity of the primary vessel to f in litres, s the number of measures of sulphurous acid required to decolorize the solution when washed out of the vessel, S the number required to decolorize 1 grm. of iodine. Then we have,

evidently, as a sufficient approximation,

$$\frac{\delta_1 V}{V} = \frac{\frac{I s}{15{\cdot}88}}{\frac{1{\cdot}4367 C p}{(1+\alpha t)760}}.$$

If we suppose ozone to be allotropic oxygen, with a relative density $e : 1$, then $\delta_1 V$ of oxygen contracts to $\frac{\delta_1 V}{e}$ on being changed into ozone. Hence, on this hypothesis,

$$\frac{\delta_1 V}{\delta V} = \frac{e}{e-1}.$$

In order to verify this method, two similar vessels were filled with pure oxygen, one containing a capsule filled with a neutral solution of iodide of potassium, the other a capsule filled with an acidulated solution of the same salt, and of precisely the same strength. The neutral solution was also introduced into the siphon tubes of both vessels. After breaking the capsules, the levels were read, and the vessels set aside for some days; at the end of which time it was found that a portion of oxygen gas had been absorbed in the primary vessel which contained the acid solution, while no change had occurred in the other. The levels were now read again, and the solution in the primary vessel analysed.

The weight of the oxygen absorbed, as calculated by the foregoing formulæ from the volumetric change, was 0·0002188 grm., while its weight deduced from the analysis was 0·0002181 grm. The close agreement between these numbers shows that the method is susceptible of considerable accuracy.

The following Table contains the results of six experiments made in the manner above described. The primary and auxiliary vessels were carefully constructed of similar dimensions, and were found, on trial, to work accurately together, so that formula (3.) was directly applicable.

	I.	II.	III.	IV.	V.	VI.
	mm.	mm.	mm.	mm.	mm.	mm.
$2x_r$.	31·5	− 3·0	−18·5	−48·5	51·0	39·0
$2(x_l+\delta x_l)$.	31·0	18·0	− 2·25	− 6·5	− 9·75	− 8·25
$2x$.	4·0	38·5	− 0·5	16·5	72·5	65·0
$2(x+\delta x)$.	−78·0	− 2·75	−55·25	− 5·0	−39·0	−27·5
C.	0·0338	0·0306	0·0288	0·0279	0·0269	0·0346
s.	9·1	5·4	5·7	5·1	4·5	4·5
	grm.	grm.	grm.	grm.	grm.	grm.
I.	0·0268	0·0684	0·0442	0·0674	0·0446	0·0621
S.	22·6	47·95	30·85	49·5	36·8	44·43
	mm.	mm.	mm.	mm.	mm.	mm.
Π.	777·0	772·5	763·0	751·0	747·2	751·0
t.	11°·0 C.	13°·45 C.	9°·1 C.	9°·8 C.	14°·0 C.	14°·7C.
$\frac{1}{H}$	0·000025	0·000024	0·000025	0·000026	0·000027	0·000036
$\frac{\delta_1 V}{\delta V}$	0·932	0·938	0·947	0·927	0·952	0·933

On comparing these experiments with the foregoing, it will be observed that they do not give exactly the same result. Interpreted as they stand, they indicate a density for ozone, if we may use the expression, more than infinite, inasmuch as the quantity of oxygen deduced from the analysis is less than that corresponding to the contraction observed. But, although every precaution was taken to avoid all sources of uncertainty, it is not improbable that this difference between the amount of oxygen deduced from the contraction and from the analysis may arise from a slight defect in some of the data, particularly as it would only involve an error of the order of $\frac{1}{1000}$th of the entire gas.

Taking the mean result of the three series of experiments as they stand, it gives, on the allotropic hypothesis, almost exactly an infinite density for ozone.

§ 5.

The commonly received statement, that the whole of a given volume of dry oxygen gas can be converted into ozone by the passage of electrical sparks, is erroneous. In repeated trials, with tubes of different forms and sizes, we found that not more than one-twelfth of the oxygen could, under the most favourable circumstances, be converted into ozone, even by the silent discharge, and a much smaller proportion by the action of sparks. But if the ozone is removed as fast as it is produced, the conversion may be carried on indefinitely. An apparatus was constructed of the form shown in fig. 7. At *a*, *b* two fine platinum wires were hermetically sealed into the glass; at *c* there was a solution of iodide of potassium, and *de* was filled with fragments of fused chloride of calcium which allowed the ozone to pass freely, but arrested the vapour of the solution; so that while the discharge always took place in pure and dry oxygen, the ozone was gradually absorbed. The volumetric change was measured by the readings of the sulphuric acid in the siphon tube *fg* sealed at *g*. The experiment was continued till five-twelfths of the oxygen (whose entire volume was about 12 cub. cent.) was absorbed, and the action was still going on. It was not considered necessary to persevere further, as the labour of turning the machine was very great. To produce the effect just mentioned, the discharge from the machine in excellent order had to be passed through the tube for twenty-four hours.

When the electrical discharge is passed through rarefied oxygen, the phenomena are apparently the same as with the gas at the common pressure of the atmosphere. We filled a vessel with oxygen and exhausted it till the pressure was equal to 1 inch of mercury, in the hope that in this rarefied state a larger portion of the oxygen might be converted into ozone than under greater pressures, but this did not prove to be the case. We intend on a future occasion to pursue this part of the inquiry, and to examine particularly the effects of the electrical discharge on oxygen in different states of rarefaction and condensation.

Ozone, obtained by electrolysis, gave results nearly similar to those already described. As the volume of the oxygen gas from which the ozone was derived could not, in the case of electrolytic ozone, be observed directly, it was estimated indirectly by placing

three vessels in line and passing the same stream of electrolytic oxygen through them all. By heating the first and last vessels to 300° C., and observing the expansion produced in each, it was easy to calculate the expansion which would have occurred in the middle vessel, if it had been exposed to similar treatment. This expansion was assumed to be equal to the contraction which occurs when ozone is produced from oxygen by means of the electrical discharge. Finally, the actual amount of ozone in the middle vessel was determined by introducing a solution of iodide of potassium, and ascertaining by analysis the amount of iodine set free. The individual experiments with electrolytic ozone did not agree so well with one another as those performed with ozone prepared by the discharge. This arose partly from the very small quantity of ozone in electrolytic oxygen, but chiefly from the irregularity in that quantity at different times, even when the current was passing very steadily, which made it difficult to ascertain with certainty the expansion due to the ozone in the middle vessel. Our earlier results, indeed, gave a measurable volume for ozone, and as a first approximation we obtained the number 4 as expressing its density*. But, by multiplying our experiments, and taking all possible precautions to ensure accuracy, we found that electrolytic ozone, like that produced by the discharge, has no appreciable volume.

Ozone is not condensed at common pressures by the cold produced by a mixture of solid carbonic acid and ether. A stream of electrolytic oxygen, passed very slowly, first through a U-tube surrounded by snow and salt, and next through a spiral tube immersed in the carbonic acid and ether bath (−76° C.), underwent no change. The ozone reactions, as the gas issued from the tube, after exposure to this low temperature, were as strong as before it entered the bath.

§ 6.

Hydrogen, prepared with care by the action of dilute sulphuric acid recently boiled on zinc, and purified by passing through three U-tubes containing corrosive sublimate in solution, hydrate of potash, and sulphuric acid, respectively, and finally, in order to remove the last trace of oxygen, through a tube filled with metallic copper heated to redness, was found not to be altered in volume, either by the sparks or by the silent discharge. It appears to be a much better conductor of electricity than oxygen.

With *Nitrogen*, prepared in the usual way by depriving atmospheric air of its oxygen by means of heated copper, the results were also negative.

Among the compound gases, *Carbonic Acid* is rapidly decomposed by the spark, slowly by the silent discharge; in both cases expansion takes place.

Cyanogen is at once decomposed by the spark with deposition of carbon (?); but presents so great a resistance to the passage of electricity, that the action of the silent discharge could not be ascertained with certainty.

Protoxide of Nitrogen is readily attacked by the spark, with the formation of hyponitric acid, whose characteristic red colour is distinctly seen. The primary result of the

* Proceedings of the Royal Society, vol. viii. p. 498, and vol. ix. p. 606.

spark action is expansion, but on allowing the gas to stand, it gradually contracts, in consequence of the absorption of the hyponitric acid gas by the sulphuric acid in the siphon tube. It is impossible to determine the precise amount of the first expansion, as a certain amount of absorption occurs at the same time; but, in one imperfect trial, the ratio between the expansion and the subsequent contraction was nearly that of 1 : 2. This corresponds to the conversion of 8 vols. of protoxide of nitrogen into 4 vols. of hyponitric acid gas and 6 vols. of nitrogen. The silent discharge appears to produce the same result as the spark, but as the action is slower, the absorption interferes with any attempt to determine accurately the primary expansion.

Deutoxide of Nitrogen presents the interesting example of a compound gas, which, under the influence both of the spark and silent discharge, undergoes, like oxygen, a diminution of volume. This is independent of the subsequent absorption of the hyponitric acid formed. This gas is remarkable for the facility with which it is decomposed by both forms of discharge. The passage of sparks for two minutes, through a tube containing about 5 cub. cent., produced a contraction of the gas to nine-tenths of its original volume, followed after some time by a contraction not quite double of the former, from the absorption of the hyponitric acid gas. On continuing to pass sparks till the decomposition was finished, and waiting till the hyponitric acid gas was completely absorbed, the residue amounted to a little more than one-fourth of the original gas. This residue consisted of a mixture of 11 vols. nitrogen and 1 vol. oxygen. It is evident that the final result is a little complicated, but there can be little doubt that the action of the spark is to convert 8 vols. of deutoxide of nitrogen into 4 vols. of hyponitric acid gas, and 2 vols. of nitrogen. This decomposition may be due to the immediate action of the discharge; or the deutoxide of nitrogen may, in the first instance, be resolved into equal volumes of nitrogen and oxygen, the latter combining as it is formed with undecomposed deutoxide.

Carbonic Oxide has given results of great interest, the investigation of which has already occupied a considerable time, although it is not yet completed. The principal facts have, however, been already ascertained, and as they present some remarkable analogies to those already described in the case of oxygen, we shall briefly allude to them here, reserving the complete investigation for a future communication.

The carbonic oxide was prepared by heating oxalic acid with an excess of sulphuric acid, and absorbing the carbonic acid by means of a strong solution of hydrate of potash. The gas, as it escaped from the end of the apparatus, did not produce the slightest turbidity in lime or baryta water, and was completely absorbed by an ammoniacal solution of the subchloride of copper.

On exposing this gas to the action of the silent discharge, a steady contraction took place, and the surface of the positive platina wire became covered with a continuous deposit of a bronze colour. After some time, a trace, but only a trace, of the same deposit appeared at the point of the negative wire. If, after a contraction of 50 millims. or 60 millims. of the siphon tube had been obtained, a few electrical sparks

were passed through the gas, the greater part of the contraction was, as in the case of oxygen, destroyed. Heat acted in the same direction, but did not restore the gas altogether to its original volume.

On continuing to pass the silent discharge, the gas continued to contract, and the deposit to increase on the positive wire. Portions of the same deposit were also scattered about the sides of the tube, being probably thrown off from the same wire. The experiment was in some cases continued till the gas had contracted to about one-third of its original volume. To effect this contraction, the machine had to be worked for sixty hours. The residual gas consisted of carbonic acid, oxygen, and undecomposed carbonic oxide. A similar deposit was obtained when the discharge took place between gold instead of platinum wires. This deposit appeared to be soluble in water. Its quantity was so small that direct analysis was altogether impossible. Its composition may, however, be determined by fixing with precision the ratio of the volumes of the carbonic acid and oxygen produced. We have succeeded in devising a method by which this analysis may be effected even with less than 0·5 cub. cent. of the mixed gases, but this part of the investigation is still unfinished.

Atmospheric Air is the only gaseous mixture which we have exposed to the action of the silent discharge. Like pure oxygen, it undergoes a diminution of volume; but the operation is more quickly terminated and the contraction is less than with that gas alone. If, after the passage of the discharge, the vessel be set aside for some hours, the contraction will be found to augment; and if the gaseous mixture be now again exposed to the action of the discharge, a further contraction will take place. On the other hand, heat destroys a portion only of the contraction at first produced. All these facts are easily explained from the simultaneous formation of ozone and one of the higher oxides of nitrogen, and the marked influence of the latter, when formed, in arresting the formation of the former. To the same cause we have succeeded in referring an apparently anomalous state of oxygen, produced by passing a stream of strong electrical sparks, for some minutes, through that gas containing a trace of nitrogen. The oxygen becomes by this treatment incapable of contracting or of changing into ozone under the action of the silent discharge, and only recovers its usual condition by exposure to heat or by standing for some hours. If the nitrogen amounts to not more than $\frac{1}{300}$th of the entire volume, this condition cannot be produced more than two or three times. At first we supposed it to be a new (passive) state of oxygen, but we have now no hesitation in referring it to the presence of a trace of hyponitric acid gas produced by the electrical sparks.

§ 7.

It is perhaps premature to attempt a positive explanation of the facts now described regarding ozone. The foregoing investigation into its volumetric relations has, for the moment, rather increased than diminished the difficulty of determining the true nature of that body. To reconcile the experimental results with the view that ozone is oxygen

in an allotropic form, it is necessary to assume that its density immensely exceeds that of any known gas or vapour; being, as we have seen, according to the first and second series of experiments (§§ 3 and 4), from fifty to sixty times that of oxygen, and according to the third series (§ 4) absolutely infinite. Even the former results would make it only six times less dense than the metal lithium, and would place it rather in the class of solid or liquid bodies than of gaseous. The question may then be fairly proposed,—Can this singular body, at common temperatures, be actually a solid or liquid substance, whose particles, in an extremely fine state of subdivision, are suspended in the oxygen with which it is always mixed? This question will scarcely, we think, admit of an affirmative answer. Not only does ozone, mixed as usual with oxygen, pass through several U-tubes containing fragments of pumice moistened with sulphuric acid, but it exhibits its characteristic reactions when left for many hours in tubes of this kind. Besides, there is not the slightest cloud visible in a tube filled with oxygen, even when one-twelfth of the gas has been converted into ozone, nor does any deposit appear after long standing.

Ozone may be formed under conditions which exclude the possibility of its containing, as a constituent, any element except oxygen, or the elements of oxygen, if that body should hereafter be shown to be compound. As has been before stated, our experiments may be reconciled with the allotropic view and an ordinary density, but still one greater than that of oxygen, if we assume that when ozone comes into contact with such substances as iodine, or solutions of iodide of potassium, one portion of it, retaining the gaseous form, is changed back into common oxygen, while the remainder enters into combination; and that these are so related to one another, that the expansion due to the former is exactly equal to the contraction arising from the latter. We do not, however, consider this supposition to be by any means probable, nor can it be easily reconciled with the results (§ 3) obtained when mercury acts on ozone.

If we consider the conditions under which ozone is formed, we shall find them to be different from those which produce allotropic modifications in other cases. Such elements, for example, as phosphorus or sulphur, are modified by the action of heat, and not by the electrical discharge. It is true, at the same time, that the destruction of ozone, or, on the allotropic view, its reconversion into oxygen, by exposure to a temperature of 270° C., is apparently analogous to that action of heat whereby common phosphorus is converted into the red variety.

Without rejecting the allotropic constitution of ozone, although the results of our volumetric experiments are certainly difficult to reconcile with it, it may not be uninstructive to consider whether the facts already known admit of a different explanation. As ozone is formed from pure and dry oxygen by the electrical discharge, if it is not an allotropic form of oxygen, the latter must be either a mechanical mixture of two or more gases, or it must be a compound gas. It is perhaps scarcely necessary to consider the former hypothesis, according to which, oxygen, in its ordinary state, would be a mechanical mixture, as atmospheric air is a mixture of nitrogen and oxygen. The contraction,

which occurs when the electrical discharge is passed through oxygen, is at first sight indeed favourable to such a supposition, inasmuch as the combination of gases is usually accompanied either by a diminution, or no change of volume. But we have not been able to discover, in its other reactions, any facts which countenance this otherwise improbable view of the constitution of oxygen gas.

Finally, it remains to be considered, whether in the formation of ozone, oxygen does not undergo a more profound molecular change than is involved in an allotropic modification, whether, in short, this supposed element may not be actually decomposed. If, for the moment, we confine our attention to the phenomena which present themselves when the electrical discharge is passed through oxygen, this attractive hypothesis will be found to furnish a simple and plausible explanation of them all. It will be observed, at once, that the conditions under which ozone is formed from oxygen by the electrical discharge, are precisely those under which other gases, known to be compound, are decomposed. The electrical current is one of very high intensity, and therefore very favourable to decomposition: when passed in the form of the silent discharge, a large contraction takes place in the volume of the gas, which is partially destroyed by a few electrical sparks, and wholly by heat. With nitrogen and hydrogen no similar effects are observed, the volume of these gases being quite unaffected by either form of discharge.

The behaviour of carbonic oxide, when exposed to the action of the silent and spark discharge, corresponds remarkably to that of oxygen; the latter form of discharge, while producing itself only a limited contraction in carbonic oxide, destroying a part of the contraction produced by the former. Again, when deutoxide of nitrogen is exposed to the action of the same agents, an immediate contraction takes place without any solid or liquid product being formed, showing that in certain cases of gaseous decompositions, the resulting gases occupy a smaller volume than the original compound.

If we assume that oxygen is resolved by the electrical discharge into a new compound (ozone), containing the same constituents as the oxygen itself, but in a different proportion, and into one of the constituents themselves, in the same manner as carbonic acid is resolved into carbonic oxide and oxygen, or nitric oxide into hyponitric acid and nitrogen, the results of our experiments will admit of an easy explanation. One of the simplest suppositions we can make for this purpose is, that two volumes of oxygen consist of one volume of U and one volume of V, united without condensation (U and V being the supposed constituents of oxygen), and that one volume of ozone consists of two volumes of U and one volume of V; and further, that by the action of heat, iodine, &c., ozone is resolved into U and oxygen.

The appearance of ozone at the positive pole in the electrolysis of water, and its formation by the agency of so active a body as ordinary phosphorus, do not seem unfavourable to its being the result of decomposition. But the same observation will not apply to its production by the action of acids on such bodies as the peroxide of barium. We certainly should not have expected to see a body derived from the decom-

position of oxygen produced under the latter circumstances, and, although the facts connected with its production in these cases have not been studied with precision, yet there appears to be no doubt that ozone is actually formed.

We must in conclusion add, that the few attempts we have made to isolate either of the supposed constituents of oxygen have failed.

We are still continuing to prosecute this inquiry, and hope on a future occasion to lay before the Society the results of further experiments which are now in progress.

Note, added July 12, 1860.

It having been suggested that a certain amount of the contraction produced by the passage of the electrical discharge through tubes containing oxygen might arise from the action on that gas of the platinum wires, or of finely divided platinum, which, as in Mr. GASSIOT's experiment, might be thrown off by the action of the discharge, we have made the following experiment, in order to ascertain whether such an action could have occurred in the conditions under which we operated. Before describing the experiment, it may be proper to state, that in the passage of the discharge of the electrical machine, there is no visible separation of metallic platinum, as in that of the discharge from the induction coil, nor other evidence of the wires being acted on; on the contrary, both the wires and tube retain their original appearance after having been frequently exposed to the alternate action of the discharge and of heat.

A vessel, of the form represented in the annexed figure, was filled with pure and dry oxygen. It differs from the tubes usually employed only by having the lower end of the reservoir drawn out into a capillary tube *a b*. The platinum wires were inserted as usual, and an auxiliary vessel of the same size and form was filled with dry air. After determining the comparative range of the two vessels, their reservoirs were exposed, in the apparatus before described, to a temperature of 300° C., in order to bring them as exactly as possible into the same condition. When they had cooled, the levels of the acid in the siphon tubes were again read, and the silent discharge was afterwards passed through the primary vessel till a contraction of twenty-seven millims. was obtained in its siphon tube. The extremity of the capillary tube of the reservoir was next cut off at *a*, and the end of the siphon tube *d*, which had the form represented in the figure, was dipped under sulphuric acid. The open end at *a* was now connected with an apparatus, which supplied a slow stream of carefully dried air, and this was allowed to pass till the ozone and oxygen originally contained in the tube were entirely displaced by the dry air. It is obvious that by this arrangement the ozone was removed, while the platinum wires and the inner surface of the tube were left in precisely the same state as after the passage of the discharge. The tube was next sealed off at *c*, by the

application of the point of a fine blowpipe flame, the current having been arrested, so as to leave the usual column of sulphuric acid in the siphon tube. In sealing it, care was taken not to allow the air in e to become heated. The vessel was again placed, along with the auxiliary, in the calorimeter, and the levels read. The ends of the siphon tubes having been first sealed, the reservoirs were exposed to 300° C. An expansion should have taken place in the primary vessel, if the platinum had retained oxygen capable of being disengaged at 300° C.; but this was not found to be the case. The change of level in its sulphuric acid siphon (corrected by the auxiliary) did not amount to 0·2 millim., a degree of accuracy rarely attainable in these experiments.

VIII. *On the Mathematical Theory of Sound.* *By the Rev.* S. Earnshaw, *M.A.*, *Sheffield.* *Communicated by Professor* W. H. Miller, *F.R.S.*

Received November 20, 1858,—Read January 6, 1859*.

In making certain investigations on the properties of the sound-wave, transmitted through a small horizontal tube of uniform bore, I found reason for thinking that the equation

$$\frac{dy}{dt}=\mathrm{F}\left(\frac{dy}{dx}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

must always be satisfied; F being a function of a form to be determined. Differentiating this equation with regard to t, we find

$$\frac{d^2y}{dt^2}=\left\{\mathrm{F}'\left(\frac{dy}{dx}\right)\right\}^2\cdot\frac{d^2y}{dx^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

which by means of the arbitrary function F can be made to coincide, not only with the ordinary dynamical equation of sound, but with any dynamical equation in which the ratio of $\frac{d^2y}{dt^2}$ and $\frac{d^2y}{dx^2}$ can be expressed in terms of $\frac{dy}{dx}$.

Equation (1.) is a partial first integral of (2.), and by means of it we shall be able to obtain a final integral of (2.), which will be shown to be the general integral of (2.) for wave-motion, propagated in one direction only in such a tube as we have supposed, by its satisfying all the conditions of such wave-motion.

It will be convenient to begin with the simplest case of sound,—that in which the development of heat and cold is neglected.

I. WAVE-MOTION WHEN CHANGE OF TEMPERATURE IS NEGLECTED.

1. The equations for this case of motion are, the dynamical equation

$$\left(\frac{dy}{dx}\right)^2\cdot\frac{d^2y}{dt^2}=\mu\frac{d^2y}{dx^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

and the equation of continuity,

$$\frac{dy}{dx}=\frac{\varrho_0}{\varrho}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

ϱ_0, p_0 are the equilibrium density and pressure at any point of the fluid; ϱ, p the same for a particle in motion; x the equilibrium distance of the same particle from a fixed plane cutting the tube at right angles; and t is the time when the same particle, being in motion, is at the distance y from the same plane; μ is the constant which connects ϱ and p by Boyle's law $p=\mu\varrho$.

* Subsequently recast and abridged by the author, but without introducing new matter.

On comparing (3.) with (2.), we find $\frac{dy}{da}\cdot F'\left(\frac{dy}{dx}\right)=\pm\sqrt{\mu}$; or, for brevity, writing α for $\frac{dy}{dx}$, we have

$$F'(\alpha)=\pm\frac{\sqrt{\mu}}{\alpha},$$

and

$$\therefore\quad F(\alpha)=C\pm\sqrt{\mu}\log_e(\alpha).$$

But as $\frac{dy}{dt}=F(\alpha)$ from (1.), it follows that

$$\begin{aligned} dy&=\frac{dy}{dx}\cdot dx+\frac{dy}{dt}\cdot dt\\ &=\alpha dx+F(\alpha).dt, \end{aligned}$$

which being integrated in the usual manner, substituting at the same time for $F(\alpha)$ its value, gives

$$\left.\begin{aligned} y&=\alpha x+(C\pm\sqrt{\mu}\log_e\alpha)t+\varphi(\alpha)\\ 0&=\alpha x\pm\sqrt{\mu}t+\varphi'(\alpha) \end{aligned}\right\}\quad\ldots\ldots\ldots\quad(5.)$$

Between these equations, if we eliminate α, we have then the integral of equation (3.).

2. From equation (4.) we see that $\alpha=\frac{\varrho_0}{\varrho}$; and if we represent by u the velocity of the particle whose place is y, we find

$$\begin{aligned} u=\frac{dy}{dt}&=C\pm\sqrt{\mu}\log_e\alpha,\\ &=C\pm\sqrt{\mu}\log_e\left(\frac{\varrho_0}{\varrho}\right); \end{aligned}$$

and

$$\therefore\quad \varrho=\varrho_0 e^{\mp\frac{u-C}{\sqrt{\mu}}}.$$

3. To determine the arbitrary constant C, we observe that $\varrho=\varrho_0$ and $u=C$ are always simultaneous equations. But the former belongs to the confines of the wave, where in fact $u=0$; and therefore $C=0$. Hence for a wave transmitted through a medium which is itself at rest beyond the limits of the wave, we have these equations*:—

$$\varrho=\varrho_0 e^{\mp\frac{u}{\sqrt{\mu}}}.\quad\ldots\ldots\ldots\quad(6.)$$

$$\left.\begin{aligned} y&=\alpha x\pm\sqrt{\mu}\log_e\alpha.t+\varphi(\alpha)\\ 0&=\alpha x\pm\sqrt{\mu}t+\alpha\varphi'(\alpha) \end{aligned}\right\}\quad\ldots\ldots\ldots\quad(7.)$$

* If x and α be eliminated between the equations (7.) and $u=\pm\sqrt{\mu}\log_e\alpha$, we shall obtain the equation

$$u=f\{y-(u\mp\sqrt{\mu})t\},$$

which was first obtained, though in a very different manner from that employed in this paper, by M. Poisson, and printed in the Journal of the Polytechnique School, tome vii. It seems not to have occurred to him, however, that by means of this equation he might effect another integration of the equations of fluid motion, and thus discover the relation between ρ and u, whereby his solution would have been completed.

Several of the properties of wave-motion, depending on the gradual change of type, which are included in this equation of M. Poisson's, were first brought forward and discussed by Professor Stokes in the Philosophical Magazine for November 1848, and by the Astronomer Royal in June 1849. In the latter

4. We have now to express these results in terms of the original genesis of the motion. Let us suppose the motion generated by a piston pushed forwards in the tube in a given manner. Let the piston at the time T (having the same origin as t) be at the distance Y from the plane of reference, and moving forwards with the velocity U; and by R denote the density of the air in contact with the piston at that moment. For all particles in contact with the piston $x=0$ (we suppose the piston to commence its motion at the origin of x). Then since at the time T the particles in contact with the piston are within the limits of the wave, equations (6.) and (7.) must be satisfied;

$$\therefore \quad \mathrm{R}=\varrho_0 \varepsilon^{\mp\frac{\mathrm{U}}{\sqrt{\mu}}}$$

$$\left.\begin{aligned} \mathrm{Y} &= \pm\sqrt{\mu}\log\alpha'.\mathrm{T}+\varphi(\alpha') \\ 0 &= \pm\sqrt{\mu}\mathrm{T}+\alpha'\varphi'(\alpha') \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (8.)$$

In these equations $\alpha'=\frac{\varrho_0}{\mathrm{R}}$, and at present we have not sufficiently connected the two systems of equations (7.) and (8.). We shall further connect them by assuming $\mathrm{R}=\varrho$, which gives $\alpha'=\alpha$; the effect of which assumption is to limit the meaning of T, Y, U as follows:—

T is the time of genesis of the density ϱ which at the time t has been transmitted to the place denoted by y;

Y is the place where the density ϱ was generated;

U is the velocity of the piston when ϱ was generated by it.

We may now write α for α', and then eliminate α, $\varphi(\alpha)$, and $\varphi'(\alpha)$ between the four equations (7.), (8.). By this means we obtain

$$y=\mathrm{Y}+(\mathrm{U}\mp\sqrt{\mu})(t-\mathrm{T}). \quad \ldots\ldots\ldots \quad (9.)$$

$$x=\mp\sqrt{\mu}\varepsilon^{\mp\frac{\mathrm{U}}{\sqrt{\mu}}}(t-\mathrm{T}). \quad \ldots\ldots\ldots \quad (10.)$$

$$\varrho=\varrho_0\varepsilon^{\mp\frac{\mathrm{U}}{\sqrt{\mu}}}=\varrho_0\varepsilon^{\mp\frac{u}{\sqrt{\mu}}}. \quad \ldots\ldots\ldots \quad (11.)$$

5. By these equations the state of a wave at any moment is connected with its genesis; and they contain in fact the complete solution of the problem of every kind of motion, in a tube, which can be generated by a piston.

6. From (11.) it appears that $u=\mathrm{U}$; that is, that the particle-velocity generated by the piston is transmitted through the medium without suffering any alteration. The same equation (11.) shows that between the density and the velocity there is an invariable relation, which is independent of the law of original genesis of the motion; so that in the same wave, or in different waves, wherever there is the same density, there will also be the same velocity.

7. One of the most obvious facts on looking at the equations just found is, that for the same genesis there are *two* values of x, two of y, and two of ϱ. The signification of

Number of the Magazine it also appears that Professor De Morgan had discovered and communicated to the Astronomer Royal two particular forms of the function F; without perceiving, however, that a slight generalization of his results would put him in the way to the integral expressed by the equations (5.).

this is, that a single disturbance generates *two* waves; and (11.) shows that for one of them ϱ is *greater*, and for the other *less* than ϱ_0. Equation (10.) shows that they are propagated in contrary directions on opposite sides of the piston, and are therefore not parts of the *same* wave.

8. In the genesis of the wave we have supposed the piston pushed forwards, that is, in the direction of $+x$. Hence for the wave generated on that side of the piston we must, as appears from (10.), take the lower sign, which in (11.) gives ϱ greater than ϱ_0. This wave we call the *positive* wave, and the wave of *condensation*. For the wave generated on the other side of the piston we must take the upper sign, which gives ϱ less than ϱ_0; and this wave we call the *negative* wave, and the wave of *rarefaction*.

9. As it will be useful to have a definition of these two waves, which shall be independent of their position with regard to the generating piston, we may state that in general,—

a *positive* wave is one in which the motions of the particles are in the direction of wave-transmission: and

a *negative* wave is one in which the motions of the particles are in a direction opposite to that of wave transmission.

10. If ϱ_1 and ϱ_2 be the densities of the air in contact with the piston before and behind at any moment, and if p_1 and p_2 be the corresponding pressures; then from (11.) we have

$$\varrho_1=\varrho_0\varepsilon^{\frac{U}{\sqrt{\mu}}}, \text{ and } \varrho_2=\varrho_0\varepsilon^{-\frac{U}{\sqrt{\mu}}},$$

and $$\therefore \quad \varrho_1\varrho_2=\varrho_0^2;$$

which may be thus expressed in words:—if a piston move in a tube, filled with air, in any manner whatever, the densities of the air in contact with it at its front and back are such that the equilibrium density is a mean proportional between them. And since $p=\mu\varrho$, we have $p_1p_2=p_0^2$, which furnishes us with a similar property for the *pressures* on the piston.

11. Since $p_1=p_0\varepsilon^{\frac{U}{\sqrt{\mu}}}$ and $p_2=p_0\varepsilon^{-\frac{U}{\sqrt{\mu}}}$, it follows that the resistance to the motion of the piston (calling S its area) is

$$(p_1-p_2)\mathrm{S}=\left(\varepsilon^{\frac{U}{\sqrt{\mu}}}-\varepsilon^{-\frac{U}{\sqrt{\mu}}}\right)p_0\mathrm{S}.$$

Hence in different gases, if p_0 be the same in all, those will offer the greatest resistance to the piston for which μ is the least.

It will be convenient from this point to consider the two kinds of waves separately.

1. *The Wave of Condensation.*

12. The equations for this wave are

$$y=\mathrm{Y}+(\sqrt{\mu}+\mathrm{U})(t-\mathrm{T})$$

$$x=\sqrt{\mu}\varepsilon^{\frac{U}{\sqrt{\mu}}}(t-\mathrm{T})$$

$$\varrho=\varrho_0\varepsilon^{\frac{U}{\sqrt{\mu}}}.$$

13. Now with respect to the genesis of this wave, we have seen that U must satisfy the same conditions as u, and Y as y. But $u=\frac{dy}{dt}$, therefore $U=\frac{dY}{dT}$: and again, as one of the equations of the general integral (7.) was obtained from the other by differentiation with regard to α, it follows that both α and U must vary continuously; and that $\frac{dU}{dT}$ must not pass through infinity; in other words, if the velocity of the piston vary it must vary continuously. Neither Y nor U must be discontinuous with regard to T. Hence there must be no discontinuity of pressure within the limits of the wave at its genesis: and if discontinuity should afterwards occur in the wave during its transmission, our equations will cease to be applicable for that part of the wave where the discontinuity has occurred. For the wave in any one position may be supposed to generate its next position; and a piston or diaphragm may at any time be supposed to act the part of the generating wave. What is necessary for the diaphragm to observe as a law of genesis must be necessary for the wave considered as the generator of its next position; and therefore the part of the wave (if any) where discontinuity occurs will be beyond the reach of our equations.

14. It has been shown that the density ϱ, which at the time t is at the distance y from the plane of reference, was generated at the time T when its distance from the same plane was Y. Hence it has been transmitted through the space $y-Y$ in the time $t-T$, and consequently the velocity of its transmission (as appears from the first equation of (12.)) is

$$\sqrt{\mu}+U.$$

15. The wave as a whole is included between two points of it for each of which $U=0$, and consequently for each of those points the velocity of transmission is $\sqrt{\mu}$. Hence the wave as a whole is transmitted with this uniform velocity. But all the parts of the wave, with the exception of its front and rear, are transmitted with velocities greater than this,—with velocities dependent on their respective densities. Hence every part of the wave, with the exception of its rear, is perpetually gaining on the front, and the result is a *constant change of type*,—the more condensed parts hurrying towards the front, with velocities greater as their densities are greater. This cannot go on perpetually without its happening at length that a *bore* (or tendency to a discontinuity of pressure) will be formed in front; which will force its way, in violation of our equations, faster than at the rate of $\sqrt{\mu}$ feet per second; and consequently in experiments, made on sound at long distances from the origin of the sound-wave, we should expect the actual velocity observed to be greater than $\sqrt{\mu}$, especially if the sound be a violent one, generated with extreme force (see art. 17).

16. We have seen that the velocity of transmission of the density ϱ is $\sqrt{\mu}+U$. Now the velocity of the particles where the density is ϱ is u, which we have shown to be equal to U. In a certain sense we may consider the velocity u to be a wind-velocity in that part of the medium, and then we have an indefinitely small disturbance at that point transmitted in that wind with the velocity $\sqrt{\mu}$ imposed upon the wind. In other

words, transmission-velocity is superimposed on particle-velocity, and in this sense transmission-velocity is everywhere the same, and equal to $\sqrt{\mu}$. A wave passes by every particle with this velocity, whatever be the particular and varying density of the medium where the particle is situated.

17. Since a wave's front cannot move faster than with the velocity $\sqrt{\mu}$, if the generating piston move faster than with this velocity, it will generate a bore; and from this we infer that a bore always moves with a velocity greater than $\sqrt{\mu}$; for wherever a bore may be situated at *any time*, we may suppose it to be *just* generated by a piston. If we write $\sqrt{\mu}$ for U, we find $p=\mu\varrho=\mu\varrho_0 s=sp_0$. Consequently if the piston press upon the resisting air with a pressure exceeding s atmospheres, a bore will be instantly formed.

I have defined a bore to be *a tendency to discontinuity of pressure*; and it has been shown that as a wave progresses such a tendency necessarily arises. As, however, discontinuity of pressure is a physical impossibility, it is certain Nature has a way of avoiding its actual occurrence. To examine in what way she does this, let us suppose a discontinuity to have actually occurred at the point A, in a wave which is moving forwards. Imagine a film of fluid at A forming a section at right angles to the tube. Then on the back of this film there is a certain pressure which is discontinuous with respect to the pressure on its front. To restore continuity of pressure, the film at A will rush forward with a *sudden* increase of velocity, the pressure in the front of the film not being sufficient to preserve continuity of velocity. In so doing the film will play the part of a piston generating a bit of wave in front, and a small regressive wave behind. The result will be a prolongation of the wave's front, thereby increasing the original length of the wave, and producing simultaneously a feeble regressive wave of a negative character.

Now all this supposes the discontinuity to have actually occurred, which, as has been said, is a physical impossibility. For actual occurrence we must therefore substitute a tendency to occur, and modify the preceding reasoning thus:—

Nature so contrives, that as the discontinuity is in its initial stage of beginning to take place, its actual occurrence is prevented by a *gradual* (not *sudden*) prolongation of the wave's front, and by the *constant* casting off, from its front in a retrogressive direction, of a long continuous wave of a negative character, which will be of greater or less intensity according as the tendency to discontinuity is more or less intense in the original wave.

The casting off of this long wave will probably manifest itself audibly as a continuous *hiss* or *rushing* sound.

Hence a sound-wave, from the moment that a tendency to discontinuity begins in its front, has the property of constantly prolonging itself in front, and by this means its front travels faster than at the rate $\sqrt{\mu}$. Those sounds also will travel most rapidly whose genesis was most violent; and gentlest sounds travel with velocities not much differing from $\sqrt{\mu}$. I should expect, therefore, that in circumstances where the human voice can be heard at a sufficiently great distance, the *command* to fire a gun, if instantly

obeyed, and the *report* of the gun, might be heard at a long distance in an inverse order; i. e. *first* the report of the gun, and *then* the word "fire*." In a slight degree, therefore, the experimental velocity of sound will depend on its intensity, and the violence of its genesis. I consider this article as tending to account for the *discrepancy* between the *calculated* and *observed* velocities of sound (which most experimentalists have remarked and wondered at), when allowance is made (as will be done in a future part of this paper) for change of temperature.

18. It seems reasonable to suppose that the audible character of a wave is in some way dependent on its type; and consequently, if this be the case, the sound undergoes a perpetual modification as the distance of transmission increases. One modification of the sound-wave is, as we have seen, the formation of a bore in front; but there is another which cannot but have some influence on its audible properties, as it corresponds to a remarkable change of type; and this takes place when the greater densities begin to overtake the less.

Now when one degree of density overtakes another, the values of y corresponding to those two densities are equal; and hence at the time t the equation

$$y=\mathrm{Y}+(\sqrt{\mu}+\mathrm{U})(t-\mathrm{T}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.)$$

will give two equal values of y for two consecutive values of T. Hence differentiating it with regard to T, remembering that t is constant, or the same for both, as is also y, we have

$$0=\mathrm{U}-(\sqrt{\mu}+\mathrm{U})+(t-\mathrm{T})\frac{d\mathrm{U}}{d\mathrm{T}},$$

or

$$t=\mathrm{T}+\frac{\mu}{\frac{d\mathrm{U}}{d\mathrm{T}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.)$$

The right-hand member of this equation is of course a continuous expression, and therefore its least or minimum value will be the value of t when the modification of type, of which we are speaking, *first begins* to take place; and because of the continuity of (13.), this modification once begun will gradually spread itself over the fore-part of the wave. Now t will be a minimum when

$$\left(\frac{d\mathrm{U}}{d\mathrm{T}}\right)^2=\mu\cdot\frac{d^2\mathrm{U}}{d\mathrm{T}^2}.$$

From this equation we may find T, the time of genesis of that part of the wave where this modification begins. Then (13.) will give t, the actual time when the modification begins; and (12.) will give the place in the tube where it begins.

19. It is perhaps impossible to say what is the audible characteristic corresponding to the wave-modification just investigated; but whatever it be, we perceive from (13.) that those sound-waves soonest begin to be affected by it for which $\frac{d\mathrm{U}}{d\mathrm{T}}$ is largest; *i. e.* those

* See Supplement to Appendix of PARRY'S Voyage in 1819–20, Art. "Abstract of Experiments to determine the Velocity of Sound."

whose genesis is most violent. And we may also consider it as proved that those sounds will retain their original characteristics the longest which are the most gently generated.

It is also quite evident from (13.) if the same cause generate sound-waves in different tubes filled with different gases, the wave will be soonest affected by the above modification in that tube which contains the gas for which μ is least.

We come now to speak of

2. *The Wave of Rarefaction.*

20. We shall obtain the equations for this kind of wave by writing $-\mathrm{U}$ for $+\mathrm{U}$ in the equations of art. 12, which is equivalent to supposing a negative wave generated on the $+y$ side of the piston. Hence the equations of a negative wave are

$$y=\mathrm{Y}+(\sqrt{\mu}-\mathrm{U})(t-\mathrm{T}),$$

$$x=\sqrt{\mu}s^{-\frac{\mathrm{U}}{\sqrt{\mu}}}(t-\mathrm{T}),$$

$$\varrho=\varrho_0 s^{-\frac{\mathrm{U}}{\sqrt{\mu}}}.$$

21. Reasoning in the same manner as in art. 14, it appears that the velocity with which the density ϱ is transmitted is

$$\sqrt{\mu}-\mathrm{U}.$$

From this it appears that, speaking generally, the velocity of transmission of every part of a negative wave is less than of every part of a positive wave. The exceptions to this statement are the front and rear, which in both kinds of waves move with the same velocity $\sqrt{\mu}$, because for those points $\mathrm{U}=0$. It is evident also that the most rarefied parts of a wave will be transmitted the most slowly, and will consequently drop continually towards the rear. Hence in this species of wave, as in the former, a constant change of type takes place; and in the end also a *negative or rarefied bore* will be formed in the *rear* of the wave.

By a process of reasoning analogous to that of art. 17, we infer that a negative sound-wave, from the moment that a tendency to discontinuity begins in its rear, has the property of constantly shortening its rear, and by this means its rear travels faster than at the rate $\sqrt{\mu}$; and also as it progresses it is constantly casting off from its rear in a regressive direction a long continuous wave of a negative character. Art. 18 also admits of easy modification to this kind of wave.

22. The velocity of transmission of a negative wave being $\sqrt{\mu}-\mathrm{U}$, and the last term of this expression admitting of arbitrary increase, it is evident that $\mathrm{U}=\sqrt{\mu}$ is a critical value, and that the part of the wave corresponding to that value of U is stationary. The corresponding value of ϱ is $\frac{\varrho_0}{e}$.

Every part of the wave where the density exceeds this travels forwards; but the parts where the density is less than this are regressive; hence a wave, as a whole, in which ϱ

begins at ρ_0, and after twice passing through $\frac{\rho_0}{e}$ ends at ρ_0, will have two stationary points in its type, viz. those where $\rho=\frac{\rho_0}{e}$. Between these points the wave will be stationary though constantly changing type; beyond them progressive.

23. But instead of supposing the piston to generate such a wave as this, let us suppose it to begin from the velocity zero, and according to any proposed law (continuous of course) increase its velocity till it becomes infinite; and let us consider the state of the medium at this moment.

Denote by A and B the places of the piston where its velocity became respectively $\sqrt{\mu}$ and infinite. Then whatever was the law of motion from A to B, and whether AB be great or small, provided it remains of finite length, the density at A will remain unchanged and equal to $\frac{\rho_0}{e}$, and the velocity of every particle as it passes by A will be equal to $\sqrt{\mu}$. The mass of air also which will rush through the section of the tube at A will be $\frac{S\rho_0\sqrt{\mu}}{e}$; and this, be it observed, cannot be made either more or less by causing the piston to move in a different manner from A to B. It is also equally independent of the law of the piston's motion before it reached A. Hence the mass of air that flows through the section at A is altogether independent of the law of the piston's motion throughout its whole course.

24. Now let us inquire what quantity of air rushes through any other section of the tube. In every part where there is motion the same relation between density and velocity obtains, viz. $\rho=\rho_0 e^{-\frac{u}{\sqrt{\mu}}}$; and consequently the quantity which rushes through any section is at the rate of

$$S\rho_0 u e^{-\frac{u}{\sqrt{\mu}}} \text{ per second.}$$

It is obvious this admits of a maximum value, which in the usual manner we find to be

$$\frac{S\rho_0\sqrt{\mu}}{e},$$

at which value $u=\sqrt{\mu}$ and $\rho=\frac{\rho_0}{e}$.

25. Hence one part of the tube cannot supply air to another part faster than at this rate; and consequently the greatest possible mass of air passes through the section at A: and it may be stated as a general property of motion through a tube, that a gas cannot be conveyed through a tube faster than at the rate of $\frac{S\sqrt{\mu}}{e}$ cubic feet per second of gas of the density ρ_0.

Hence the escaping powers of different gases through equal tubes are proportional to the velocities with which they respectively transmit sound.

26. Since this result is independent of the law of velocity of the air, both before and after passing the section A, we are entitled to say that air cannot rush through a pipe of finite length, even into a vacuum, faster than at the rate of $\frac{S\sqrt{\mu}}{e}$ cubic feet per

second. The length of the pipe seems to be a matter of perfect indifference, and may be nothing more than a hole through a partition of finite thickness.

27. Since one part of a tube cannot supply air to, nor convey air away from, another part, A, faster than at the maximum rate, it is easy to see that if the pipe be supposed of finite length, which conveys air into a vacuum, the velocity in every part of the pipe will soon be the same throughout, and equal to $\sqrt{\mu}$, and density everywhere equal to $\frac{\varrho_0}{e}$.

From this it would appear that the rate of discharge into a vacuum, which has generally been supposed to be that which is due to the height of the homogeneous atmosphere, is in reality that which is due to the $\left(\frac{1}{2e^2}\right)$th part only; that is, to little more than the fifteenth part of it; but this requires correction for change of temperature.

28. If the generating piston move forward and then backward, so as to generate a positive wave followed continuously by a negative wave, they will not separate; for, as we have seen, they are each transmitted, as wholes, at the same rate $\sqrt{\mu}$. But the main body of the positive wave will gradually advance in the type towards its front, and that of the negative wave fall back towards its rear; and consequently for the purposes of audibility the central part of the compound wave, between the front of the positive and the rear of the negative wave, will become so attenuated that it may be considered of little audible effect, after the waves have been in existence a sufficient length of time to allow the formation of bores. The compound wave will therefore have a tendency to produce the audible effect of two separate waves, separated by an interval of space nearly equal to its whole length. If therefore the length of such a compound wave be sufficiently great, it will ultimately produce *two* distinct sounds separated by a very brief interval of time.

29. If the generating piston move backward and then forward, so as to generate a negative wave followed continuously by a positive wave, the positive and negative bores will destroy each other as rapidly as they are formed. This, however, supposes the positive and negative portions of the original compound wave to be equal. If one exceed the other in quantity of motion, the result will be a little modified. A compound wave of the kind supposed in this article will therefore be entirely devoid of bores, and the sound corresponding to it will be free from that harshness which is probably the audible character of a bore.

30. If there be a continuous succession of positive and negative waves, constituting one long compound wave, such a wave will produce a continuous even sound, called a musical note, probably owing its sweetness in some degree to the property just mentioned; and as every negative portion is succeeded by a positive portion, and every positive by a negative, the length of each portion will remain unchangeable, whatever be the distance through which the compound wave travels. Hence the pitch of a musical note cannot change by distance of transmission.

31. Suppose a portion of the tube to be filled with air of a different kind from that which fills the first part. Let p'_0 ϱ'_0 μ' be the quantities for this air which correspond to p_0 ϱ_0 μ of the former; and to prevent the two airs or gases from mixing, let them be supposed to be separated by an impenetrable film without weight and inertia. Then as there is equilibrium in the tube before the wave is generated, we have

$$p_0 = p'_0.$$

Let now a wave be generated in the first medium and transmitted towards the second; then when it has reached the common boundary of the media, the velocities of the particles in contact with the film on both sides will always be equal. Let U′ be this velocity at any moment, and U the velocity which the film would have had at that moment, if the second medium had been the same as the first. Then U − U′ is the velocity lost by the particles of the first medium by the resistance due to their contact with the film. In other words, this velocity has been impressed on the particles of the first medium by the resistance of the film, in the reflex direction. This gives rise to a reflex wave in the first medium, which we may consider superimposed on the wind of the original wave. And consequently if p be the pressure at the film due to the original wave, the pressure when this reflex wave has been superimposed, *i. e.* the actual pressure at the film, is $= p\varepsilon^{\frac{U-U'}{\sqrt{\mu}}}$, which $= p_0\varepsilon^{\frac{2U-U'}{\sqrt{\mu}}}$, $\therefore p = p_0\varepsilon^{\frac{U}{\sqrt{\mu}}}$.

But if we now turn to the other side of the film, the velocity U′ has been impressed upon the particles of the second medium in contact with the film; and hence the pressure of those particles on the film

$$= p'_0\varepsilon^{\frac{U'}{\sqrt{\mu'}}} = p_0\varepsilon^{\frac{U'}{\sqrt{\mu'}}};$$

and consequently, as the pressures on the two sides are equal, we have

$$\frac{U'}{\sqrt{\mu'}} = \frac{2U - U'}{\sqrt{\mu}}.$$

Hence the velocities of the particles at the film, for the *incident*, *reflected* and *refracted* waves, are respectively proportional to

$$\sqrt{\mu} + \sqrt{\mu'},\ \sqrt{\mu} - \sqrt{\mu'},\ \text{and}\ 2\sqrt{\mu'}.$$

There is nothing new in these formulæ, except that they are here deduced without supposing the motions small.

II. WAVE MOTION WHEN CHANGE OF TEMPERATURE IS NOT NEGLECTED.

32. The heat developed by that change of temperature which is produced by the sudden alteration of density due to the passage of a wave, is probably taken account of by using the following equation as that which connects pressure and density,

$$\frac{p}{p_0} = \left(\frac{\varrho}{\varrho_0}\right)^k;$$

k being the ratio of the specific heat of the gas under a constant pressure, to its specific heat under a constant volume. The dynamical equation takes for this case the following form to be used instead of that in art. 1,

$$\left(\frac{dy}{dx}\right)^{k+1}\cdot\frac{d^2y}{dt^2}=k\mu\cdot\frac{d^2y}{dx^2}.$$

This equation being integrated as explained in art. 1, gives

$$\left.\begin{aligned} y&=ax+\left(\mathrm{C}\mp\frac{2\sqrt{k\mu}}{k-1}\alpha^{-\frac{k-1}{2}}\right)t+\varphi(\alpha)\\ 0&=ax\pm\sqrt{k\mu}\alpha^{-\frac{k-1}{2}}t+a\varphi'(\alpha)\end{aligned}\right\}\quad\ldots\ldots\quad(14.)$$

33. From these we obtain

$$u=\frac{dy}{}=\mathrm{C}\mp\frac{2\sqrt{k\mu}}{k-1}\alpha^{-\frac{k-1}{2}},$$

$$=\mathrm{C}\mp\frac{2\sqrt{k\mu}}{k-1}\left(\frac{\varrho}{\varrho_0}\right)^{\frac{k-1}{2}}.$$

For the same reasons as before we shall suppose $u=0$ and $\varrho=\varrho_0$ to be simultaneous equations; which gives

$$\mathrm{C}=\pm\frac{2\sqrt{k\mu}}{k-1},$$

and

$$\therefore\quad\left(\frac{\varrho}{\varrho_0}\right)^{\frac{k-1}{2}}=1\mp\frac{(k-1)u}{2\sqrt{k\mu}}.\quad\ldots\ldots\quad(15.)$$

This equation gives the relation between density and velocity; from which that between pressure and velocity is easily found.

34. The general integral (14.) may be expressed in terms of the original genesis precisely in the same manner as was employed in art. 4; and the result is

$$y=\mathrm{Y}+\left(\frac{k+1}{2}\mathrm{U}\mp\sqrt{k\mu}\right)(t-\mathrm{T}).\quad\ldots\ldots\quad(16.)$$

$$x=\mp\sqrt{k\mu}\left(1\mp\frac{k-1}{2\sqrt{k\mu}}\mathrm{U}\right)^{\frac{k+1}{k-1}}(t-\mathrm{T}).\quad\ldots\ldots\quad(17.)$$

$$u=\mathrm{U},\text{ and }p=p_0\left(\frac{\varrho}{\varrho_0}\right)^k.\quad\ldots\ldots\quad(18.)$$

These equations, with (15.), are those from which the properties of the motion are to be deduced. The degree of modification of former results required by these formulæ will be in most cases sufficiently evident, and need not therefore to be particularly pointed out.

35. The result of art. 10 takes the following form—

$$\varrho_1^{\frac{k-1}{2}}+\varrho_2^{\frac{k-1}{2}}=2\varrho_0^{\frac{k-1}{2}};$$

and that of art. 11 the following—

$$(p_1-p_2)\mathrm{S}=\mathrm{S}p_0\left\{\left(1+\frac{k-1}{2\sqrt{k\mu}}\mathrm{U}\right)^{\frac{2k}{k-1}}-\left(1-\frac{k-1}{2\sqrt{k\mu}}\mathrm{U}\right)^{\frac{2k}{k-1}}\right\}.$$

36. From (16.) it appears that the velocity of transmission of the front and rear of either a positive or negative wave is $\sqrt{k\mu}$; but the velocity of transmission of that part of the wave of which the density is ϱ, is, for a positive wave,

$$\sqrt{k\mu}+\frac{k+1}{2}\mathrm{U};$$

and for a negative wave,

$$\sqrt{k\mu}-\frac{k+1}{2}\mathrm{U}.$$

The part of these expressions to which the bore is due is the term $\frac{k+1}{2}\mathrm{U}$; and as k is known to be greater than unity, this is greater than U; and consequently change of temperature hastens the formation of a bore, and also renders the property of art. 16 inapplicable here.

37. As in the case of a negative wave the equation (15.) involves a negative term, it is manifestly possible for the piston, in generating a negative wave, to move so quickly as to leave a vacuum behind it. The least velocity with which this can happen is

$$\frac{2\sqrt{k\mu}}{k-1},$$

which for common air is about 5722 feet per second. But it is necessary to notice, that in this and similar extreme results, we are hardly justified in supposing k to be constant up to such high velocities.

38. The expression $\mathrm{S}\varrho u$ is a maximum (see art. 24) when

$$u=\frac{2\sqrt{k\mu}}{k+1},$$

which in the case of common air is equal to about 904 feet per second; and the corresponding density is

$$\varrho=\left(\frac{2}{k+1}\right)^{\frac{2}{k-1}}\varrho_0;$$

or, for common air, about $\frac{2}{5}\varrho_0$.

Hence no gas can rush through a pipe faster than at the rate of

$$\sqrt{k\mu}\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}\mathrm{S}$$

cubic feet per second.

39. The change of temperature due to the transmission of a wave through an elastic medium has been taken account of, by assuming a law different from that of BOYLE, to connect pressure with density (art. 32).

If we generalize the law by assuming

$$p=\varphi\left(\frac{\varrho_0}{\varrho}\right),$$

the dynamical equation takes the form

$$\frac{d^2y}{dt^2}=-\frac{1}{\varrho_0}\cdot\varphi'\left(\frac{dy}{dx}\right)\cdot\frac{d^2y}{dx^2}.$$

If now we assume

$$(\mathrm{F}'\alpha)^2=-\frac{\varphi'\alpha}{\varrho_0},$$

the integral of the dynamical equation will be

$$\begin{cases} y=\alpha x+(\mathrm{C}\pm\mathrm{F}\alpha)t+f\alpha, \\ x=\mp\mathrm{F}'\alpha.t-f'\alpha, \end{cases}$$

with $\alpha=\frac{\varrho_0}{\varrho}$, and $u=\mathrm{C}\pm\mathrm{F}\alpha=\mathrm{C}\pm\mathrm{F}\left(\frac{\varrho_0}{\varrho}\right)$.

40. These equations are true of any motion which can be generated by a piston moving subject to the laws of continuity. See art. 13. The last shows that the relation between velocity and density is independent of the law of genesis of the motion. The medium may be, as a whole, in motion with the uniform velocity $\mathrm{C}\pm\mathrm{F}(1)$, and the motion of the particles caused by the motion of a piston will be superimposed on this. For convenience we shall suppose the medium as a whole at rest, and $\therefore\ \mathrm{C}\pm\mathrm{F}(1)=0$.

If there be a point, or any number of points, within that part of the medium which is in motion for which $\varrho=\varrho_0$, for all such points $\alpha=1$, and the equation

$$x=\mp\mathrm{F}(1).t-f'(1),$$

which is always true for all such points, shows that at those points x changes its value at the rate of $\mathrm{F}(1)$ feet per second, *i. e.* the front of the wave travels at the rate of

$$\left\{-\frac{\varphi'(1)}{\varrho_0}\right\}^{\frac{1}{2}} \text{ feet per second,}$$

which is constant, and depends not at all on the law of genesis, but only on the assumed relation between pressure and density, and not on the *general* value of even that, but only on its limiting value when $\varrho=\varrho_0$. Now many different forms of the function φ may give the same limiting value; and consequently all the media corresponding to these various forms of φ will transmit a wave, as a whole, with the same velocity. Hence if the relation between pressure and density be given, the wave-velocity may be instantly deduced from the expression $\left\{-\frac{\varphi'(1)}{\varrho_0}\right\}^{\frac{1}{2}}$, or from its equal,

$$\left\{\frac{dp}{d\varrho}\right\}_0^{\frac{1}{2}};$$

using the subscript 0 to signify that after the differentiation has been performed ϱ_0 is to be written for ϱ.

41. Since $u=\mathrm{C}\pm\mathrm{F}\left(\frac{\varrho_0}{\varrho}\right)$, by differentiation we obtain

$$\frac{du}{d\varrho}=\mp\frac{1}{\varrho}\left(\frac{dp}{d\varrho}\right)^{\frac{1}{2}}.$$

42. And if c denote the velocity of transmission of the density ϱ, then we have

$$c=C\pm F\left(\frac{\varrho_0}{\varrho}\right)\mp\frac{\varrho_0}{\varrho}F'\left(\frac{\varrho_0}{\varrho}\right)=u\mp\left(\frac{dp}{d\varrho}\right)^{\frac{1}{2}};$$

consequently

$$\frac{dc}{d\varrho}=\mp\frac{1}{\varrho}\cdot\frac{d}{d\varrho}\left(\varrho^3\frac{dp}{d\varrho}\right)^{\frac{1}{2}}.$$

Now the former of these equations shows that unless the term $\left(\frac{dp}{d\varrho}\right)^{\frac{1}{2}}$ be constant, the property of the superposition of wave-transmission on particle-velocity, proved in art. 16, does not hold good. But if it be constant, then $p=\mu\varrho+\mu'$; which is the general relation between pressure and density when that principle of superposition holds good. Hence, as mentioned in art. 36, the development of heat puts an end to this property in all known gases.

43. In the case of negative waves we may institute a method of reasoning similar to that employed in arts. 23 *et seq.*, and arrive at analogous results. We shall also find that, taking $c=\left(\frac{dp}{d\varrho}\right)^{\frac{1}{2}}-u$ for this case, the maximum value of $S\varrho u$ will occur in that section of the tube where $c=0$; from which it follows that at that section

$$u=\left(\frac{dp}{d\varrho}\right)^{\frac{1}{2}};$$

which is always possible and finite. Hence may be determined the limit to the quantity of a gas that can pass through a pipe in a given time, even into a vacuum.

44. The expression in art. 42 for $\frac{dc}{d\varrho}$ shows that c is in general a function of ϱ, so that in general there will be a constant change of type. In one case, however, there will be no change of type. This will take place when $\frac{dc}{d\varrho}=0$, that is when $\varrho^3.\frac{dp}{d\varrho}$ is constant. Assume for this case

$$\varrho^3\frac{dp}{d\varrho}=B;$$

$$\therefore p=A-\frac{B}{\varrho}.$$

This equation expresses the nature of the medium which is distinguished by the property, that it transmits waves without change of type. And if we pass from this to the dynamical equation, we find

$$\frac{d^2y}{dt^2}=\frac{B}{\varrho_0^3}\cdot\frac{d^2y}{dx^2}.$$

Now it has been usual to reduce the equation (3.) to this form for the purposes of approximation; but the process appears to be allowable only so far as the equation $p=A-\frac{B}{\varrho}$ may be taken to be a physical approximation to BOYLE's law $p=\mu\varrho$. To me it does not seem to be an allowable approximation; and consequently I do not consider the solution of the dynamical equation, which has been obtained by this means, to be

applicable to the problem of sound at all. Many *analytically* approximate forms might be invented and used for BOYLE's law, and each would have its peculiar physical attributive effects on the sound-wave; and we might thus, by adopting first one and then another of these analytically approximate laws, invent *ad libitum* an inexhaustible list of properties of the sound-wave which have no real existence where BOYLE's law is strictly true. From which therefore it would seem to be a necessary consequence, that an equation between p and ρ must not only be *analytically* but also *physically* approximative, in order that the results deduced from it may be accepted as real approximations to the true laws of nature.

45. By means of the expressions for $\frac{du}{d\rho}$ and $\frac{dc}{d\rho}$, we may not only discover the properties of motion in a tube without having recourse to the usual equations, when the relation between ρ and p is known, but we may also solve many inverse problems.

Also, if the tube be filled with a medium of such a nature that the relation between p and ρ changes continuously from point to point, or is different in different parts, yet if $\left(\frac{dp}{d\rho}\right)_0$ has the same value everywhere, waves will travel through the tube with a uniform velocity.

If the nature of the medium should vary slowly and continuously, the velocity of the wave-transmission would be known, from the equations given above, by integration.

46. If, through the partial radiation of heat, or from any other cause, the dynamical equation should take the form

$$\frac{d^2y}{dt^2}=f\left(\frac{dy}{dx},\ \frac{dy}{dt}\right).\frac{d^2y}{dx^2},$$

we must integrate it as before by assuming

$$\frac{dy}{dt}=\mathrm{F}\left(\frac{dy}{dx}\right);$$

which gives

$$(\mathrm{F}\alpha)^2=f(\alpha,\ \mathrm{F}\alpha).$$

This equation being integrated will furnish the form of F; and then the integral of the proposed dynamical equation will be

$$\begin{cases} y=\alpha x+(\mathrm{C}\pm\mathrm{F}\alpha)t+\varphi\alpha, \\ x=\mp\mathrm{F}'\alpha.t-\varphi'\alpha, \end{cases}$$

which does not present any new difficulty.

IX. *On the Lines of the Solar Spectrum.*

By Sir David Brewster, *K.H., D.C.L., F.R.S. L. & E., and Dr.* J. H. Gladstone, *F.R.S.*

Received January 26,—Read February 23, 1860.

In a paper published in the Transactions of the Royal Society of Edinburgh for 1833, Sir David Brewster stated that by various means he had examined the lines of the solar spectrum, and those produced by the intervention of nitrous acid gas, and had delineated them on a scale four times greater than that employed in the beautiful map of Fraunhofer. Some portions also, which were more particularly studied, had been drawn on a scale twelve times greater. "Fraunhofer," he continued, "has laid down in his map 354 lines, but in the delineations which I have executed, the spectrum is divided into more than 2000 visible and easily recognized portions, separated from each other by lines more or less marked, according as we use the simple solar spectrum, or the solar and gaseous spectrum combined, or the gaseous spectrum itself, in which any breadth can be given to the dark spaces." None of these drawings, however, were published at the time. Frequent observations were continued during the years 1837, 1838, and 1841; and now, after a lapse of many years, the various delineations, having been collated and arranged by Dr. Gladstone, form the principal diagrams in the Plate accompanying this paper.

Fig. 1 of Plate IV. represents the lines observed when the sun was at a considerable altitude above the horizon, and its light was examined by means of a good prism and telescope. The spectrum is delineated on so large a scale that it was necessary to divide it into two portions, the upper diagram representing the part between the least refrangible end and the line designated F 7, the lower diagram the part between F 7 and the most refrangible end. On a comparison with Fraunhofer's large map*, the principal lines and features will be easily recognized; but it will be seen that every portion of the spectrum contains lines wanting in the earlier drawing, and that parts which Fraunhofer has marked by one line are resolved into groups of bright spaces alternating with dark lines. The figure of the spectrum extends at the more refrangible or violet end to about the same distance as that of the Bavarian philosopher, but it exhibits a considerable extension at the red or less refrangible end. The principal lines are indicated by those letters, A, *a*, B, C, &c., which were assigned to them by him, and the larger intermediate lines are marked by numbers, 1, 2, 3, &c., beginning afresh on the more refrangible side of each letter; so that any one of these may be expressed by a combination of a letter and numeral; as, for instance, C 6, a

* In his "Bestimmung des Brechungs- und Farbenzerstreuungs-Vermögens verschiedener Glasarten."

remarkable line in the orange, of which much will be said hereafter. The extreme violet is lettered, both in this and in a map to be subsequently described, by that continuation of the alphabet which has been adopted by M. BECQUEREL*. It was necessary to indicate in some similar manner the newly published, though not newly discovered, lines at the red end of the spectrum; and as the alphabet has not been appropriated by M. BECQUEREL beyond P, and it is not likely that further research will largely extend the spectrum in that direction, it was thought safe to take the end of the alphabet, and denoting the first strongly-marked line before A by Z, to work backwards into those slightly refrangible rays, which have been as yet unresolved by human vision. Some of the dark spaces of the spectrum are of an appreciable breadth, in which case they are represented as bands; and where the observation of a line was indistinct or uncertain, it is marked by an interrupted instead of a continuous line.

The light less refrangible than A is red but extremely faint, so faint indeed, that few observers of the spectrum have perhaps ever seen it; and the only drawing hitherto published of lines in it, appears to be in a map of the solar spectrum by M. MATTHIESSEN of Altona†. He represents a few lines which, on comparison with fig. 1, may be identified as the band anterior to Y, Y itself, and the band Y 1. In order to map the lines and bands in this portion of the prismatic image, Sir DAVID BREWSTER was obliged to take extraordinary precautions. The telescope was lined with black velvet, in order to exclude any reflected light; a low power was employed; the slit was made about the 8th or 10th of an inch wide, and the eye of the observer was washed with water to cleanse the fluid that lubricates the cornea‡. The most prominent line in this space is that marked Y.

The red space between A and B is marked by FRAUNHOFER merely by a bundle of lines midway between the two, and designated *a*. It is indeed difficult to resolve the light that extends from A to *a*, but between *a* and B lines and bands are easily perceptible. This space is delineated not only in fig. 1, but on a larger scale in fig. 2, while fig. 3 is a still more magnified view of the bundle of lines that constitute *a*. The succession of pale thin bands between A and *a* 1, represented in fig. 2, were only distinctly seen on one occasion; and to the drawing Sir DAVID BREWSTER appends the remark, "their exact places and breadths require to be better fixed." They usually present themselves to the observer as two or three broader bands, filling up nearly the whole space. The series of bands marked by faint lines between *a* 3 and B, is a peculiar feature of this part of the spectrum.

Between B and C little can be detected with certainty beyond the four lines previously observed by FRAUNHOFER. The orange space between C and D is far richer; but immediately beyond the double line D is a yellow space of considerable breadth marked by only one, and that a faint line, and this is the most luminous portion of the whole spectrum.

* Bibl. Univ. de Genève, xl.

† Referred to in Compt. Rend. xix. p. 112.

‡ See Comptes Rendus, 1850, tom. xxx. p. 579.

The green space between E and F was made the object of special study, and a separate map of it on a scale twelve times that employed by FRAUNHOFER is given in fig. 4, while fig. 5 represents, on a still larger scale, the lines included within what is ordinarily denominated the triple line *b*.

The blue space between F and G is that of which the delineations appear the least trustworthy; indeed there is some discrepancy among the drawings of the lines between F 18 and F 27. The violet space from G to H is probably deserving of greater confidence. The sparse lines beyond H seem to extend to the further limit of BECQUEREL's group L, which, with the group I, is faintly indicated.

In the summer of 1858 Dr. GLADSTONE examined the two extremities of the solar spectrum where FRAUNHOFER's map is manifestly deficient; and as these are the portions where there is least light, he made his observations on very bright days about midsummer, and at noon, consequently when the sun was at about its highest in the latitude of London. The instrument of the Rev. BADEN POWELL, described and figured in the British Association Report for 1839, was employed, and a good prism of flint-glass having an angle of 45°. The light of the sun was reflected from the quicksilvered mirror of a heliostat; and a blue cobalt glass was placed in front of the eyepiece of the telescope. This latter precaution is necessary in order to intercept, or greatly reduce in brilliancy, the orange, yellow, and green rays; for although the telescope takes only a part of the prismatic image into the field of view at a time, it will still happen that, however pure the glass of the prism may be, and however carefully cross-lights are prevented, some of the middle rays will be irregularly dispersed, and will mix with the red or lavender; and when the sun is shining brightly into the instrument, these rays will be in sufficient quantity to render it a matter of great importance that they should be stopped by cobalt glass. The results of these observations are given in fig. 6, which is on the same scale as FRAUNHOFER's spectrum, or one-fourth of that adopted in fig. 1.

From this map it is evident that the appearance of lines and bands between A and B is not confined to periods of the day, or latitudes, where the sun is at no great height above the horizon, although none, except the group *a*, are delineated in the Munich diagram. It will presently be seen, however, that they become much more visible when the sun's light traverses a larger portion of our atmosphere. Light was perceived by Dr. GLADSTONE for a considerable space anterior to A, but no lines were distinguishable in it, on account probably of the inferiority of his apparatus to that employed by Sir DAVID BREWSTER, whose drawings also had not been seen or heard of by him when he made these observations.

On comparing this map in its delineation of the rays beyond H with the drawings of M. BECQUEREL* and Professor STOKES†, it will be at once evident that it contains the lines marked by them as far as it extends, besides many finer ones. Yet the three maps represent three different phenomena: that of BECQUEREL the lines and spaces where there is no chemical action; that of Professor STOKES the lines and spaces where

* Bibliothèque Univ. de Genève, xl. † Philosophical Transactions, 1852.

no fluorescence is produced in bisulphate of quinine, or similar bodies; while this represents those where there is no effect on the organ of vision. Professor STOKES mentions in a note to his paper, that he had "succeeded, by a particular arrangement, in seeing so far into the 'lavender' rays as to make out the groups of fixed lines m, n, p by means of light received directly into the eye, and even to perceive light beyond that." The m, n of his drawing answer to the M and N of M. BECQUEREL'S map, and his p is nearly coincident with its termination. The figure of M. MATTHIESSEN extends at least as far as the fluorescent spectrum of Professor STOKES, but it does not clearly appear how it has been obtained.

Professor PIAZZI SMYTH, during his recent astronomical experiment on the Peak of Teneriffe, had an opportunity of analysing the light of the sun when seen through a smaller amount of atmosphere than has fallen to the lot of any other investigator. He has incorporated such observations made near noon-day in the account of his experiment*, but unfortunately his apparatus was imperfect. His statements amount to this: that "comparing a high sun-spectrum at the sea-level with a similar one at Alta Vista 10,702 feet high, both observed direct, it was found that while in the former the spectrum terminated immediately beyond H, and the two bars of H were nebulous, in the latter the spectrum extended beyond H to three times the distance of its bars asunder: the two said bars also lost all their nebulosity, being clearly resolved into their component lines; many fine clear lines were seen between them, and many appeared nebulously in the space beyond." He gives other good reasons also for the conclusion that "we may assume that there is a much greater amount of the more refrangible rays in the sun's light in the upper, than in the lower regions of the atmosphere." To his drawings of the spectrum at evening, reference will be hereafter made.

Absorption by the Atmosphere.

The absorbent power exercised by the earth's atmosphere on the more refrangible rays already alluded to, is extremely evident when the sun is shining through a long reach of air, as at his rising or setting. Everyone has remarked that under such circumstances the luminary acquires a more or less red colour. This is due to the total absorption of the lavender and violet rays, the greater or less absorption of the blue and green, and the diminution of the yellow and perhaps the orange rays, whilst the red pass apparently unimpeded through the deepening atmosphere, and from the absence of the dazzling yellow, reveal themselves with their characteristic lines to the eye even when unshielded by any coloured medium. This is also the case, to a certain extent, when the sun at any altitude shines through mist or smoke; and the same result may be at any time obtained by placing in the path of the rays a vessel of water with which a few drops of milk have been mixed.

It is scarcely necessary to say, that, though the visible spectrum becomes shorter as the

* Philosophical Transactions, 1858, pp. 503 to 507.

sun sinks, there is no real contraction of its several parts, the distance between the fixed lines measuring precisely the same at different hours.

The red sun is often attended with a blue sky; the diffused light, in fact, always exhibits portions of the spectrum which are wanting in the direct rays. This may give rise to a singular phenomenon. There is a green glass coloured by means of copper and iron which has the power of absorbing the whole of the red and orange rays, but allowing others to penetrate. If the landscape be viewed through this, all the ordinary objects are seen with tolerable distinctness, though of a greenish or bluish colour, but anything purely red is extinguished; and it has happened to Dr. GLADSTONE, on examining the western sky near sunset with such a glass, that he has seen the various configurations of the clouds and of the horizon perfectly, whilst the sun itself was so little visible that its presence would not have been detected, unless it had been specially sought for. No black space is produced in this experiment; for of course that portion of the sky immediately between the solar disk and the spectator is sending diffused light like the parts adjacent.

Atmospheric Lines.

Beyond this absorption of the more refrangible rays, another and more remarkable phenomenon presents itself when the sun descends towards the horizon and shines through a rapidly increasing depth of air. Certain lines which before were little if at all visible, become black and well-defined, and dark bands appear even in what were formerly the most luminous parts of the spectrum. This has been observed both at sunrise and sunset; and it is not necessary that the luminary should be just on the horizon, or that the absorption of the more refrangible rays should be very complete; indeed these atmospheric lines have been seen when H and *k* were easily distinguishable, and light was perceptible far beyond. Fig. 7 is a map of these lines and bands, compiled from the independent drawings of the two authors, which agree very closely. In calling them "atmospheric," nothing more is meant to be expressed by the term than the mere fact that these lines or bands become much more visible as the sun's rays pass through an increasing amount of atmosphere. Sir DAVID BREWSTER first observed them, and gave a verbal description of them in the paper already referred to*, but his more exact and extended observations were made subsequently. In the least refrangible part of the spectrum which was first observed by him, the bands X 3, Y 1, Y 3, and Z 1 become very dark as the sun sets, and assume the appearance of broad black bands, supporting on each side the finer lines Y and Z. A becomes very wide even when the sun is at a considerable altitude, its aspect being that represented in fig. 8, which is on the same scale as fig. 3; and gradually the lighter portions on each side of the black line become quite dark, and the series of lines before it are converted into a dark band, so that it presents the appearance of two black spaces divided by a narrow luminous space; but as the sun sets this light also disappears, and it becomes one uniform expanse of darkness. The group *a* becomes much deeper in shade, but not uniformly so, for the bright spaces between the bands are not absorbed. In general the shaded parts between A and B

* Edinburgh Philosophical Transactions, vol. xii. pp. 529, 530.

become rather less luminous as the sun descends; but the greatest effect is observable in the narrow band α 8, the nearest to B, the appearance of which at that time is represented in fig. 9, where the scale is double that of fig. 2. C and most of the lines between it and C 6 are deepened; and the last-mentioned line is particularly noticeable, as it begins to intensify when the sun is at a considerable altitude; indeed in Great Britain it is very evident during winter at any hour of the day. When the sun is about to set, or when it is just rising, it is one of the most strongly marked lines in the whole spectrum. C 15 increases to a black band, C 16 becomes more evident than before, and the double line D is very strongly developed; D 1 deepens in shade; and at about D 2 commences a band, marked by the Greek letter δ in the diagram (fig. 7), which is one of the most characteristic features of the prismatic image of light that has passed through a long space of air. It is discernible in the diffuse light of a dull day at any hour; it is that which Professor W. A. MILLER observed manifesting itself on the occasion of a thunder shower*; and it becomes evident in the direct solar rays when the luminary is several degrees above the horizon: from its occurrence in a most luminous part of the ordinary spectrum, and from its great breadth, it intercepts a large amount of light, even at that time; and when the sun is just setting, it becomes a broad space of almost total darkness. It appears to cover a larger amount of the image in the direction of E, as it deepens in shade. It is succeeded by other bands, ε and ζ, and by a line η. The latter becomes very prominent, and from its vicinity to the comparatively faint line E, which is not perceptibly deepened by the atmosphere, has sometimes been mistaken for E itself. Beyond δ there are several remarkable bands, especially those designated in the map by the letters ι and $\varkappa$. F itself seems to become nebulous; and between it and G appear seven bands, λ, μ, ν, ξ, o, π, ϱ: the representation of the six last given in the map is on the authority of one single observation and drawing by Sir DAVID BREWSTER. It is but rarely that this part of the spectrum can be seen at sunset; and the portion beyond G is so seldom visible, and when seen is so faint, that no atmospheric lines or bands have been descried in it.

Allusion has already been made to the fact that the band δ is easily recognizable in diffused light; and this is more or less true, as might be expected, of the other bands and lines. Indeed the western sky after sunset affords a favourable opportunity for studying those in the more luminous parts of the spectrum. If the sky be red, C, C 6, D, and δ generally appear as four very black bands; if it be yellow, they are not so well defined. The various colours of the clouds also afford a great variety of appearance, but not so much in the character of the dark spaces, as of the luminous image which they intersect. There seems to be a difference in the visibility of these bands at different times, which is not readily accounted for; thus on October 29, 1837, at Allerly, near Melrose, at the instant of sunset the luminous sky gave a spectrum in which C 6, though distinctly seen, was not black, nor was D, nor δ, while the line B was *very broad* and deep. For thirty-seven minutes after sunset this black B was discernible; but even then, and indeed until the twilight had gone, the forementioned bands, usually so

* Philosophical Magazine, August, 1845, p. 85.

prominent, did not appear either black or wide. On October 31, again, the atmospheric lines were not so dark as usual, while the rays beyond C 10 had evidently suffered a considerable absorption. On neither of these occasions was there much colour in the sky; but that the phenomena did not depend on either the absence or presence of humidity in the atmosphere, is evident from the fact that on the earlier date there was a keen frost, while on the later day the weather was wet, the thermometer being 38° F. at the time of observation. That moisture, however, has some influence in the production of these bands, is shown by the effect of a fog on the solar radiations; thus on November 20, 1858, at 10 o'clock A.M., at London, the sun loomed red through a mist, and a prismatic analysis of its light showed *a* and B with extreme distinctness, and the characteristic C 6, δ, and η.

When the sun's rays traverse a mixture of milk and water, though they are dispersed and absorbed to a large extent, especially at the more refrangible end of the spectrum, these atmospheric lines are in no way exhibited; a proof, if additional proof be needed, that they are not owing to the mere reduction of the light.

It is a most beautiful and striking sight to observe the gradual appearance of these characteristic lines as the sun descends towards the horizon. Professor PIAZZI SMYTH remarked it; and from his elevated position on the Peak, he had the peculiar advantage of observing the sun when it had sunk beneath the astronomical horizon, even to the depth of 1°·1. In his drawings* it is curious to trace the gradual darkening of *a* and B, and the intermediate lines, of what he calls the "growing" line beyond C, and of the dark band that follows D. In the drawing made by him when the sun was at an altitude of −1°·1, the bands between C 6 and *b* appear to occupy a still larger space than in the diagram compiled from the observations in Scotland and England. This, of course, is in accordance with what might have been anticipated.

Measurements.

The following are the refractive indices of the principal lines of the spectrum, atmospheric or otherwise, as determined for the flint-glass of which the prism employed by Dr. GLADSTONE is composed:—

A	1·6069	F	1·6292
a	1·6087	G	1·6404
B	1·6104	G 33	1·6464
C	1·6122	H	1·6501
C 6	1·6139	K	1·6513
D	1·6162	I	1·6548
End of δ	1·6192	L	1·6567
End of ζ	1·6219	2nd of group M	1·6589
E	1·6234	5th of group M	1·6614
b	1·6249	1st of group N	1·6642

* Philosophical Transactions, 1858, Plate XXXV.

It may be well to state that the angular measurements from which these numbers were calculated, showed a proportion between the different lines almost identical with that represented in the drawings of Sir DAVID BREWSTER, and also in the map of M. MATTHIESSEN of Altona.

Light reflected from the Moon.

As the light of the moon is only that of the sun reflected from her surface, it might be anticipated that it would exhibit the same fixed lines; and so indeed it does. The authors of this paper, like other observers*, have remarked this. Sir DAVID BREWSTER saw distinctly the lines in the lunar spectrum from B to near H, and placed it on record that they were *exactly the same* as those in the solar spectrum. Dr. GLADSTONE observed the same, but with him the prismatic image appeared to terminate at the less refrangible end, just on the C side of B, and at the more refrangible end it seemed to be suddenly cut off by the line H; but whether this was precisely the case could not be determined by measurement, as there was not sufficient light in the field of view at the extremities of the spectrum to see the cross-wires of the telescope. When the moon sank towards the horizon, the more refrangible rays were found to be partially absorbed, while the lines C and D became very strongly marked; C 6 made its appearance in its proper position—as determined by angular measurement—and the band δ came distinctly into view.

It is worthy of remark, that there is nothing in the reflecting surface of the moon, or in her atmosphere (if she have any), which produces fresh bands of absorption in the solar light, at least as far as prismatic analysis has yet revealed.

Many observers have remarked that there are parts of the prismatic image which give rise to different sensations of colour according to their intensity. Thus in the spectrum of direct sunlight a broad space appears yellow, while in that of diffused light the same colour is sometimes restricted perhaps to the narrow bright band between D and D 2, the adjoining rays appearing orange on the one side, and green on the other. Striking illustrations of this were obtained during the examinations of the spectrum afforded by moonlight. Sir DAVID BREWSTER saw the green space extending a little beyond F; Dr. GLADSTONE found the portion between G and H, which is usually violet, to be strictly analogous in colour to those "lavender" rays beyond H, which he was then studying; and another party, to whom he showed the lunar spectrum, remarked at once the abnormal colour of these rays, but designated them "grey," and that without knowing that Sir JOHN HERSCHEL had applied the same term to the almost invisible extreme rays of the solar image. In like manner, Sir DAVID BREWSTER on one occasion in describing a spectrum of the western sky after sunset, adds the note,—"There is a slight tinge of *blue* close to F, but the general colour beyond it is *violet*."

* For FRAUNHOFER's observations see GILBERT's Ann. vol. lxxiv. p. 375.

Lines produced by Absorbent Media.

In the paper already referred to*, Sir DAVID BREWSTER described the remarkable series of dark lines and bands which make their appearance in the spectrum when nitrous acid gas is interposed between the prism and the source of light, whether that be the sun or a burning lamp. He mentions also the circumstance that heating the gas produces the same increase in the number and breadth of these lines as an increased thickness of the gaseous stratum itself does. From his drawings made about that time, fig. 10 is compiled. It is on half the scale of fig. 1, and the principal lines of the solar spectrum are inserted, with a view of identifying the position of the nitrous bands. These bands are numbered in the figure, beginning not with 1 but with 10, so that any future observer publishing a map with those lines in the orange and red spaces, which require a greater thickness of gas, or a higher temperature to develope them, may continue the numbers also in the same backward direction.

Almost immediately after the publication of this effect of nitrous acid fumes on light, Professor W. H. MILLER, of Cambridge, announced the discovery of different series of lines caused in the spectrum by the interposition of bromine and iodine vapour, and euchlorine gas†. These lines differ wholly from the preceding. Subsequently Professor W. A. MILLER, of King's College, investigated the subject, and published‡ not merely a description, but coloured drawings also of the lines and bands of absorption produced by iodine, bromine, chlorous acid, nitrous acid, and perchloride of manganese. His delineation of the nitrous bands does not profess to be very accurate, and differs considerably in detail from the much fuller drawings that are united together in fig. 10, partly perhaps because he employed a sufficiently dense stratum of gas to bring out lines in the red, and to intercept nearly the whole of the violet rays.

It was observed by Sir DAVID BREWSTER in the same paper§, that a solution of oxalate of chromium and potash has the remarkable property of giving rise to a sharp and narrow black band in the prismatic image. This band coincides with the bright space between the solar bands *a* 6 and *a* 7. Analogous absorption bands have been remarked when light has been transmitted through solutions of other salts; for instance, blue compounds of cobalt, salts of the protoxide and of the peroxide of uranium, permanganate of potash, and salts of didymium, beside such substances as chlorophyll, alizarine, and purpurine‖.

Origin of Lines.

The origin of these fixed lines and bands in the solar spectrum is a question still unresolved. It may be conceived—

* Phil. Trans. Edinb. vol. xii. p. 522. † Phil. Mag. 1834. ‡ Ibid. August, 1845, p. 81.

§ P. 525. See also Philosophical Transactions, 1835, p. 92.

‖ See the papers of Sir JOHN HERSCHEL, Phil. Trans. Edinb. ix.; of Sir DAVID BREWSTER, Phil. Trans. Edinb. xii. p. 538; of Professor STOKES, Philosophical Transactions, 1852, pp. 487, 517, 522, 558, and Quart. Journ. Chem. Soc. 1859, p. 219; and of Dr. GLADSTONE, Quart. Journ. Chem. Soc. 1857, pp. 79 and 219, and Phil. Mag. Dec. 1857.

1st. That the light when emitted from the photosphere itself is deficient in these rays. This was evidently the idea of FRAUNHOFER.

2nd. That they are due to absorption by the sun's atmosphere.

3rd. That they are due to absorption by the earth's atmosphere.

Or it is conceivable that some of these lines and bands have one origin and some another, though it seems more natural to refer them all to one cause.

The first supposition, that they are originally wanting in the light itself, scarcely admits of a positive proof.

If the second supposition, that they (or some of them) are due to the sun's atmosphere, be true, it may be expected that the light which comes through a minimum amount of such atmosphere would present less appearance of these lines than that which has traversed a longer portion. During the eclipse of the sun in March 1858, Dr. GLADSTONE made preparations for determining whether the light coming merely from the thin edge of his disk would be different in this respect from the ordinary sunlight, but unfortunately clouds prevented the experiment being carried out on that occasion*. However, by other contrivances, each of the authors came independently to the conclusion that there is no perceptible difference in this respect between the light from the edge and that from the centre of the solar disk.

That the earth's atmosphere has much to do with the manifestation of these lines is beyond all question, and the analogy of such gases as nitrous acid, or bromine vapour, suggests the idea that they may originate wholly in the air that encircles our globe. Nor does the observation that an increased depth of air affects some lines greatly, and others little, if at all, militate against the supposition that they are all due to the same absorbent medium; for such a band as No. 44 of the nitrous acid spectrum (fig. 10) will appear much the same whether a thin or a thick stratum of the gas has been interposed, while the band No. 10 will only make its appearance when the stratum is deep. Again, a thin stratum of a uranium salt in solution shows a dark band in the greenish-blue space, and on increasing the thickness this dark band remains almost the same in width, while four new bands make their appearance in the blue portion, and the violet is absorbed. This question, however, appears susceptible of an *experimentum crucis*. Were we to take any artificial light, and examine it by a prism through a sufficient length of air, we ought to see the fixed lines developing themselves, if they be due to the atmosphere, or entirely absent, if otherwise. This was tried by Dr. GLADSTONE. The lighthouse at Beachy Head exhibits thirty oil-lamps on a triangular stage, each furnished with a large parabolic silvered reflector. The light of ten of these lamps at once is thus thrown into one beam, which as the apparatus revolves sweeps the horizon, and is visible about as far as any artificial light in existence. On the nights of August

* After this communication had been sent to the Society, Dr. GLADSTONE was made acquainted with the fact that the same idea had occurred previously to Professor FORBES, and that he had determined by the annular eclipse of May 15, 1836, that the light from the edge of the solar disk is identical in this respect with ordinary sunlight.—Phil. Mag. vol. ix. p. 522.

31 and September 1, 1859, it was seen from Shoreham and Worthing, at the distance of twenty-five and twenty-seven miles respectively, and across the sea, like a star of the second magnitude, but of an orange colour. On examining it by the prism and telescope, it was resolved into a thread of light of a pale yellow colour, shading off into red at one end and into green at the other, while absorbent glasses showed that the spectrum did not extend either way beyond C and F. No lines were detected. The result therefore is unfavourable to the above supposition; for though twenty-seven miles of atmosphere, even at its densest, could not be expected to produce what are described above as "atmospheric lines," D and *b* might reasonably have been looked for; yet on account of the faintness of the light, and the difficulty of distinguishing with certainty a minute break in a flickering luminous thread, no great reliance should be placed on this negative result. The stars promise the best means of solution, since their light traverses precisely the same terrestrial atmosphere as that of the sun does. FRAUNHOFER saw, as was antecedently probable, some new lines of absorption in the spectra of certain fixed stars, while he recognized the line D in Pollux and Procyon, and the lines D and *b* in Capella and Betalgeus. Yet he did not observe these familiar lines in the spectra of Sirius and Castor; but it may be fairly open to doubt whether this did not arise from the extreme difficulties attending the observation. The experiments of the present authors in this direction, though they have had the use of powerful telescopes, have not led to any definite conclusions as to these lines, but they have both noted other remarkable phenomena of absorption, especially on examining the spectra of the coloured stars*.

The origin of the fixed lines of the solar spectrum must therefore still be considered an undecided question†.

Luminous Bands in Artificial Lights.

While the spectra of some artificial lights exhibit all the coloured rays gradually shading one into the other, those of some other lights consist of a series of luminous bands separated by dark spaces; and one of the most remarkable facts is this, that these luminous bands sometimes coincide with the dark lines of the solar spectrum. Thus the intense yellow light of the soda-flame is well known to have the same refrangibility as D; and this ray is prominent also, according to W. A. MILLER, in the flames of lime, strontia, baryta, zinc, iron, and platinum, and, according to ANGSTROM, in the electric flames of every metal examined by him. But the most remarkable case occurs when carbon or sulphur is burnt in nitre. The brilliant light, when analysed by a prism, exhibits a spectrum about as long as that of the sun at noon day, but marked by bright lines, among which three are particularly prominent, respectively violet, yellow, and red in colour. The violet ray is not quite so refrangible as the solar H, but the yellow is coincident with D, and the red with A, while between the red and yellow

* For Sir D. BREWSTER's observations see his 'Optics,' Ed. 1853, p. 94.

† Wherever they originate it is possible that they may be phenomena of interference, as Sir DAVID BREWSTER has observed analogous lines and bands in portions of decomposed glass consisting of numerous films.

appear at times fainter lines, one of which coincides with B, and a bundle sometimes appears in about the position of *a*.

Fig. 11 represents a series of lines, principally orange, that appear in the spectrum of a spirit-lamp flame, on the wick of which nitrate of strontia has been placed. It is from a drawing by Sir DAVID BREWSTER, and its position in the spectrum is indicated by the ordinary letters. The yellow line coincident with D is very prominent.

P.S. Much additional light has been thrown on these luminous bands, and their relation to the dark lines of the solar spectrum, by the recent labours of continental observers.

X. *On the Electric Conducting Power of Alloys.* *By* A. Matthiessen, *Ph.D.* *Communicated by Professor* Wheatstone.

Received November 17,—Read December 22, 1859.

The method employed for the following determinations is described in the Philosophical Magazine (February 1857). The precautions taken were the following:—

1. Almost all the wires were determined in naphtha (rock-oil), and the temperature observed.

2. They were all soldered to two thick copper wires, whose resistances were known and brought into the calculations.

3. Two separate wires of each alloy, of different diameters, were generally pressed or drawn (as it was thought possible that in pressing out the wires they might contain alloys of different compositions, as, for instance, when the amalgams are pressed, we find that at first almost pure mercury comes out of the small hole), and two determinations were made with wires cut from the first, and a third from the second wire.

4. The higher bismuth alloys were pressed in very fine wires, about 0·2 millim. diameter, in order to obtain concordant results*.

5. The diameters of the wires were measured at each end, and generally also in the middle; pieces of the wire, after the resistance had been determined, being bent at the ends, so that they were at right angles to each other, and to the intermediate portion of the wire, in order that the diameter might be measured in two directions, which are also at right angles with each other, by laying the wire with its two ends vertical in succession. The brittle wires were broken in short lengths, a number of them measured, and the mean taken of the values so found.

6. A number of normal wires of different lengths were used, so that when the resistances were great, equally accurate results could be obtained.

7. Those bismuth-alloys which expand on cooling, so much that the liquid metals break through the crust and form globules on the surface, were recast in small pieces, so that one whole piece was used for pressing the wire; for it is very possible that the globules which form on the surface have a different composition from the part which first solidifies.

All the wires which were not pressed were hard drawn, and they were compared with a hard drawn pure silver wire, whose conducting power, taken at 0°†, =100.

To save space only the mean of the three determinations will be given; the bismuth-tin series, however, is given in full, and serves as a fair specimen of the accuracy of the experiments; and when no concordant results could be obtained, a mark (+) will be

* Philosophical Transactions, 1858.

† All the temperatures are in the Centigrade scale.

put to the alloy, and the value for its conducting power is the mean of several determinations. A greater accuracy than that which has been obtained could not be expected, on account of the great difficulty of pressing or drawing a wire perfectly round and of a homogeneous composition. Those alloys which were drawn into wire will be underlined, and when the whole series was drawn, it will be mentioned in a foot note.

TABLE I.

Bismuth-Tin Series.

Alloy.	Conducting power, I. wire.	Temperature.	Conducting power, II. wire.	Temperature.	Conducting power, III. wire.	Temperature.	Mean of	
							Conducting power.	Temperature.
Bi_{200} Sn	1·08	25°·0	1·08	25°·2	1·07	25°·3	1·08	25°·2
Bi_{90} Sn	0·420	27·0	0·414	27·2	0·421	27·2	0·418	27·1
Bi_{60} Sn	0·262	26·2	0·267	26·4	0·262	26·4	0·264	26·3
Bi_{44} Sn	0·246	26·7	0·244	26·9	0·244	26·9	0·245	26·8
Bi_{30} Sn	0·256	23·6	0·253	23·8	0·256	24·8	0·255	24·1
Bi_{10} Sn	0·352	24·4	0·357	24·8	0·360	24·8	0·356	24·7
Bi_8 Sn	0·513	29·6	0·515	29·8	0·510	29·7	0·513	29·7
Bi_4 Sn	0·630	29·4	0·629	29·6	0·637	29·8	0·632	29·6
Bi_2 Sn	1·03	30·0	1·02	29·9	1·06	29·9	1·04	29·4
Bi Sn	2·22	28·3	2·23	28·5	2·28	28·7	2·24	28·5
Bi Sn_2	3·93	25·6	3·97	25·7	3·97	25·8	3·96	25·7
Bi Sn_4	5·84	23·0	5·85	24·2	5·83	24·4	5·84	23·8
Bi Sn_6	7·02	27·8	7·12	28·0	6·99	28·0	7·04	27·9
Bi Sn_8	7·79	24·8	7·82	24·8	7·84	25·0	7·82	24·9
Bi Sn_{44}	10·22	24·0	10·43	24·4	10·57	24·3	10·41	24·2

Determinations made with pressed and drawn lead wires gave exactly the same values.

The following alloys, viz. the two last silver-lead, the two last silver-tin, the two last gold-tin, and all the gold- and silver-copper alloys, were made in the manner which will be described in a paper "On the Conducting Powers of Copper," &c., by Dr. M. HOLZMANN and myself.

The alloys used for the determinations were those whose specific gravities have been determined*; and the metals composing them may be classed under two heads, viz.—

Class A. Those metals which, when alloyed with one another, conduct electricity in the ratio of their relative volumes.

Class B. Those metals which, when alloyed with one of the metals belonging to Class A, or with one another, do *not* conduct electricity in the ratio of their relative volumes, but *always* in a lower degree than the mean of their volumes.

To Class A. belong lead, tin, zinc, and cadmium.

To Class B. belong bismuth, mercury, antimony, platinum, palladium, iron, aluminium, gold, copper, silver, and in all probability most of the other metals.

I shall now say a few words—

1. On the conducting power of the metals employed.

2. On the conducting power of the alloys made of the metals of Class A. with one another.

* On the Specific Gravity of Alloys in this volume, p. 177.

3. On that of alloys made of the metals of Class A. with those of Class B.
4. On that of alloys made of the metals of Class B. with each other.
5. General conclusions.

1. *On the Conducting Power of the Metals employed.*

They have all been redetermined, and the values found the same as those given in my paper "On the Electric Conducting Power of the Metals*," with the exception of gold (see Appendix at the end of this paper) and copper ("On the Electric Conducting Power of Copper," &c.). These values are given in Table II.

TABLE II.

Specific gravities used for the calculation of the result.	Metal.	Conducting power.	Equivalent used.
10·468	Silver	100 at 0°	108
8·921†	Copper	93·16 at 19·4	
19·265	Gold	72·88 at 21·3	197
——	Aluminium.....	33·76 at 19·6	
7·148‡	Zinc	27·39 at 17·6	32·6
8·655	Cadmium	22·10 at 18·8	56·0
——	Iron§	14·14 at 20·4	
——	Palladium	12·64 at 17·2	
7·294	Tin	11·45 at 21·0	58
——	Platinum	10·53 at 20·7	
11·376	Lead	7·77 at 19·3	103·7
6·713	Antimony	4·29 at 18·7	122·3
13·573	Mercury.....	1·63 at 22·8	100
9·822	Bismuth	1·19 at 13·8	208

2. *On the Conducting Power of the Alloys made of Metals belonging to Class A. with one another.*

The mean of the three determinations found for the conducting power of these alloys is given in Table III., and also their calculated conducting powers, supposing that the conducting powers of the metals employed take part in that of the alloy in the ratio of their relative volumes‖.

* Philosophical Transactions, 1858.

† Taken from GMELIN'S 'Chemistry,' as no concordant results could be obtained.

‡ Prepared by distilling zinc which contained no arsenic. Three determinations, the pieces being refused between each, gave $\left\{\begin{matrix} 7{\cdot}144 & 15°{\cdot}5 \\ 7{\cdot}150 & 14°{\cdot}4 \\ 7{\cdot}149 & 15°{\cdot}0 \end{matrix}\right\}$ mean 17·148 at 15°.

§ The iron used in making the alloys was precipitated galvano-plastically by a very weak current from a solution of pure protosulphate of iron.

‖ $P=\frac{vc+v'c'}{v+v'}$, where P= conducting power of the alloy.
v and v'= the volumes of the two metals used.
c and c'= their respective conducting powers.

Table III.

Lead-Tin Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the	
		Conducting power.	Temperature.	Volume.	Diff.
	Pb				
Pb_6 Sn	87·31	8·13	18·6	8·22	−0·09
Pb_4 Sn	82·09	8·28	9·1	8·43	−0·15
Pb_2 Sn	69·63	8·71	16·0	8·89	−0·18
Pb Sn	53·41	9·29	15·0	9·48	−0·19
Pb Sn_2	36·43	10·15	15·9	10·11	+0·04
Pb Sn_4	22·28	10·57	16·2	10·63	−0·06
Pb Sn_6	16·04	10·78	18·6	10·86	−0·08

Tin-Cadmium Series.

	Sn				
Sn_6 Cd	88·06	12·72	22·1	12·72	
Sn_4 Cd	83·10	13·23	22·3	13·25	−0·02
Sn_2 Cd	71·08	14·44	20·2	14·53	−0·09
Sn Cd	55·14	16·14	20·9	16·23	−0·09
Sn Cd_2	38·06	18·36	19·6	18·05	+0·31
Sn Cd_4	23·50	19·62	20·3	19·60	+0·02
Sn Cd_6	17·00	20·42	20·5	20·29	+0·13

Tin-Zinc Series.

	Sn				
Sn_6 Zn	91·28	12·66	21·3	12·84	−0·18
Sn_4 Zn	87·46	13·32	20·0	13·45	−0·14
Sn_2 Zn	77·71	15·28	20·0	15·00	+0·28
Sn Zn	63·56	17·35	19·9	17·26	+0·09
Sn Zn_2	46·58	19·67	21·1	19·96	−0·29
Sn Zn_4	30·36	22·28	20·1	22·55	−0·17

Cadmium-Zinc Series.

	Cd				
Cd_6 Zn	89·49	22·48	19·4	22·65	−0·17
Cd_4 Zn	85·02	22·86	20·3	22·90	−0·10
Cd_2 Zn	73·94	23·45	21·3	23·48	−0·03
Cd Zn	58·66	23·87	22·3	24·29	−0·42
Cd Zn_2	41·50	24·13	22·2	25·19	−1·06
Cd Zn_4	26·19	25·15	20·3	26·00	−0·85
Cd Zn_6	19·12	25·86	20·0	26·38	−0·52

Lead-Cadmium Series.

	Pb				
Pb_6 Cd	89·43	8·38	21·9	9·29	−0·91
Pb_4 Cd	84·93	8·99	23·0	9·93	−0·94
Pb_2 Cd	73·81	10·20	18·5	11·52	−1·32
Pb Cd	58·49	12·61	21·8	13·72	−1·11
Pb Cd_2	41·33	14·63	21·2	16·18	−1·55
Pb Cd_4	26·05	17·70	20·7	18·37	−0·67
Pb Cd_6	19·02	18·98	21·4	19·38	−0·40

Although the values found for some of the alloys of cadmium-zinc and lead-cadmium do not agree exactly with their calculated conducting powers, yet we see from their curves which are drawn on Plate V.*, that they do not vary much from straight lines, and we shall see further on that we cannot group them with either of the other classes.

3. *On the Conducting Power of Alloys made from the Metals belonging to Class A. with those of Class B.*

The values found for the alloys of this class are given in Table IV., together with their calculated conducting powers.

TABLE IV.

Bismuth-Lead Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the volume.
		Conducting power.	Temperature.	
	Bi			
Bi_{160} Pb	99·73	0·904	25°·8	1·208
Bi_{128} Pb	99·66	0·610	23·8	1·213
Bi_{100} Pb	99·57	0·428	24·8	1·218
Bi_{88} Pb	99·50	0·310	25·6	1·223
Bi_{70} Pb	99·39	0·291	25·0	1·23
Bi_{48} Pb	99·11	0·270	21·3	1·25
Bi_{30} Pb	98·59	0·261	22·9	1·28
Bi_{24} Pb	98·24	0·257	24·1	1·31
Bi_{20} Pb	97·89	0·271	24·0	1·33
Bi_{14} Pb	97·01	0·289	23·9	1·39
Bi_{12} Pb	96·54	0·303	23·5	1·42
Bi_{10} Pb	95·87	0·313	21·3	1·46
Bi_{8} Pb	94·89	0·357	22·6	1·53
Bi_{6} Pb	93·31	0·405	21·5	1·63
Bi_{4} Pb	90·28	0·521	20·0	1·83
Bi_{2} Pb	82·29	0·859	19·9	2·35
Bi Pb	69·91	1·41	19·2	3·17
Bi Pb_2	53·74	2·09	22·2	4·23
Bi Pb_4	36·74	2·87	22·5	5·35
Bi Pb_6	27·91	3·47	21·3	5·93
Bi Pb_8	22·50	4·02	21·7	6·29
Bi Pb_{10}	18·85	4·35	20·9	6·53
Bi Pb_{24}	8·83	5·55	24·4	7·19
Bi Pb_{100}	2·27	7·03	24·0	7·62

Antimony-Lead Series.

	Sb			
Sb_2 Pb	80·00	2·86	24·2	4·99
Sb Pb	66·67	3·31	26·3	5·45
Sb Pb_2	50·00	3·93	23·4	6·03
Sb Pb_4	33·33	4·72	24·1	6·61
Sb Pb_6	25·00	5·52	26·1	6·90
Sb Pb_{10}	16·66	6·03	25·4	7·19
Sb Pb_{20}	9·09	6·64	25·5	7·45
Sb Pb_{50}	3·85	7·09	23·7	7·64

* The dots on the lines indicate the points at which the experiments were tried.

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TABLE IV. (continued.)

Lead-Gold Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the volume.
		Conducting power.	Temperature.	
	Pb		°	
Pb_{20} Au	94·69	5·84	25·4	11·23
Pb_{10} Au	89·91	4·31	23·0	14·34
Pb_8 Au	87·70	3·76	26·1	15·78
Pb_6 Au	84·25	2·83	19·7	18·03
Pb_4 Au	78·10	3·01	22·3	22·04
Pb_2 Au	64·07	3·59	16·8	31·18

Lead-Silver Series.

	Pb			
Pb_{50} Ag	97·69	7·91	25·3	9·81
Pb_{20} Ag	94·64	8·06	24·3	12·71
Pb_8 Ag	87·60	8·49	26·6	19·20
Pb_4 Ag	77·94	8·98	26·1	28·11
Pb_2 Ag	63·86	10·68	15·6	41·10
Pb Ag	46·90	11·69	16·5	56·73
Pb Ag_2	30·64	15·63	13·9	71·74
Pb and Ag*	1·39	47·62	23·8	98·72
Pb and Ag*	0·89	67·13	23·4	99·18

Bismuth-Tin Series.

	Bi			
Bi_{200} Sn	99·81	1·08	25·2	1·21
Bi_{50} Sn	99·58	0·418	27·1	1·23
Bi_{60} Sn	99·38	0·264	26·3	1·25
Bi_{44} Sn	99·15	0·245	26·8	1·28
Bi_{30} Sn	98·76	0·255	24·1	1·32
Bi_{10} Sn	96·38	0·356	24·7	1·56
Bi_6 Sn	94·11	0·513	29·7	1·79
Bi_4 Sn	91·42	0·632	29·6	2·07
Bi_2 Sn	84·19	1·04	29·9	2·81
Bi Sn	72·70	2·24	28·5	3·99
Bi Sn_2	57·19	3·96	25·7	5·59
Bi Sn_4	40·05	5·84	23·8	7·35
Bi Sn_6	30·81	7·04	27·9	8·29
Bi Sn_8	25·04	7·82	24·9	8·89
Bi Sn_{44}	5·73	10·41	24·2	10·86

Antimony-Tin Series.

	Sb			
Sb Sn_4	36·42	6·07	20·7	8·84
Sb Sn_6	27·63	6·56	20·4	9·47
Sb Sn_{10}+	18·64	7·21	22·4	10·12
Sb Sn_{20}	10·28	7·70	27·4	10·71
Sb Sn_{40}	5·42	8·49	27·0	11·06
Sb Sn_{100}	2·24	9·62	25·7	11·29
Sb Sn_{200}	1·13	9·98	27·9	11·37

* These two alloys were analysed; the silver in them was determined

TABLE IV. (continued.)

Tin-Gold Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the volume.
		Conducting power.	Temperature.	
	Sn.			
Sn_{100} Au.....	98·73	11·11	23·6	12·23
Sn_{50} Au.....	95·89	9·97	23·8	13·98
Sn_{18} Au.....	93·33	9·18	24·2	15·55
Sn_{12} Au.....	90·32	7·76	19·8	17·40
Sn_8 Au.....	86·15	6·13	19·2	19·96
Sn_6 Au.....	82·35	4·98	21·7	22·30
Sn_5 Au.....	79·54	4·28	21·3	24·03
Sn_4 Au.....	75·67	5·12	22·3	26·41
Sn_3 Au.....	70·00	8·86	21·0	29·90
Sn_2 Au.....	60·87	14·27	18·1	35·51
Sn Au.....	43·75	8·88	15·9	46·03
Sn Au_2	28·00	5·18	15·0	55·72
Sn and Au *	2·11	13·12	21·4	71·58
Sn and Au *	1·17	19·59	18·8	72·16

Tin-Silver Series.

	Sn			
Sn_{150} Ag.....	99·28	11·37	21·9	12·08
Sn_{50} Ag.....	97·47	11·46	20·3	13·69
Sn_{35} Ag.....	96·52	11·46	20·3	14·53
Sn_{24} Ag.....	94·87	11·57	20·3	15·99
Sn_{18} Ag.....	93·28	11·56	20·1	17·40
Sn_{12} Ag.....	90·25	11·53	20·1	20·09
Sn_6 Ag.....	82·23	12·23	23·3	27·19
Sn_4 Ag.....	75·51	12·58	19·8	33·14
Sn_2 Ag.....	60·66	14·35	20·6	46·29
Sn and Ag †	2·01	23·95	20·6	98·22
Sn and Ag †	0·93	35·71	20·7	99·17

Here we find some curious results, viz. that some alloys conduct less than either of the metals composing them; and on looking at Plate VI.‡, on which the curves of the conducting powers of the alloys belonging to this class are represented, we see how rapidly the conducting power decreases on the one side of the curve with small per-centages of the other metal; and if we follow it to the other side, we find how little the conducting power of the metal of Class A. is affected by large per-centages of the metal of Class B. To this fact I shall return when I come to the general conclusions.

The lead and tin alloys, with a large proportion of antimony, could not be made into wire, on account of their extreme brittleness and hardness. The alloys of lead with a large proportion of gold were so excessively hard, brittle and infusible, that they could

* The gold in these alloys was determined.

† The amount of silver in these alloys was determined.

‡ On the same Plate, in order to show the decrement of the conducting power of the bismuth alloys, parts of the bismuth-lead and bismuth-tin curves are drawn on a scale in which silver is taken as 1000.

not be pressed; even gold alloyed with 0·25 per cent. of lead could not be drawn; it appears to be perfectly rotten. Most of the gold-lead alloys which were determined were much more brittle than glass. The gold-tin alloys, although just fusible enough to press, were yet excessively brittle. Silver with lead and tin could only be pressed or drawn within certain limits; and where no wires could be obtained, that portion of the curve is denoted by dotted lines. Nearly all the gold alloys, especially those rich in gold, were made with gold which had been precipitated by algaroth powder, &c. (see Appendix).

In Table V. are given some experiments made with certain commercial metals alloyed with pure tin or lead. The values are the mean of two determinations; and from the values found we see that they all belong to Class B, as they all conduct *less* than the calculated values.

TABLE V.

	Mean of	
	Conducting power.	Temperature.
		C°
Hg Sn	3·78	22·0
Pb alloyed with 10 per cent. Pd	6·22	24·5
Sn alloyed with 10 per cent. Pd	9·06	24·2
Pb alloyed with 10 per cent. Pt	5·18	21·4
Sn alloyed with 10 per cent. Pt	9·37	21·1
Sn alloyed with 2·5 per cent. Fe* ...	9·71	20·5
Zn alloyed with 10 per cent. Al	24·02	24·5

4. *On the Conducting Power of Alloys made of the Metals of Class B. with one another.*

The values found for these alloys are given in Table VI., and their curves on Plate V.

TABLE VI.

Bismuth-Gold Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the volume.
		Conducting power.	Temperature.	
	Bi		C°	
Bi_{99} Au	99·47	1·01	24·0	1·57
Bi_{49} Au	98·81	0·998	21·6	2·04
Bi_{20} Au	97·64	1·09	19·9	2·88
Bi_3 Au	94·31	1·25	21·9	5·27
Bi_4 Au	89·23	1·42	22·6	8·92
Bi_3 Au	80·55	1·82	13·7	15·14
Bi Au	67·43	2·95	14·3	24·55

* The iron in this alloy was determined; the numbers placed by the side of the metals denote the percentage by weight.

TABLE VI. (continued.)

Bismuth-Silver Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the volume.
		Conducting power.	Temperature.	
	Bi			
Bi_{200} Ag	99·76	1·12	21·3	1·43
Bi_{50} Ag	99·04	1·11	21·4	2·14
Bi_{24} Ag	98·01	1·14	21·4	3·16
Bi_{12} Ag	96·10	1·32	19·9	5·05
Bi_8 Ag	92·49	1·65	21·6	8·61
Bi_4 Ag	89·15	1·78	20·3	11·92
Bi_2 Ag	80·42	2·45	20·1	20·54
Bi Ag	67·23	3·30	21·4	33·56
Bi Ag_2	50·64	4·66	22·4	49·95
Bi Ag_4	33·91	8·08	20·3	66·49
Bi and Ag*	2·33	47·87	22·9	97·70

* The amount of silver was determined.

Gold-Copper Series.

	Au			
Au and Cu	97·72	46·66	19·1	73·34
Au and Cu	95·67	33·01	19·4	73·75
Au and Cu	91·54	22·45	17·9	74·58
Au and Cu	83·83	15·35	20·3	76·16
Au and Cu	73·15	12·66	19·6	78·32
Au and Cu	53·20	11·45	17·8	82·37
Au and Cu	38·05	12·49	20·1	85·44
Au and Cu	31·07	14·00	17·1	86·91
Au and Cu	19·36	19·86	16·9	89·23
Au and Cu	11·43	28·74	19·5	90·84
Au and Cu	9·06	33·16	17·0	91·32
Au and Cu	3·53	53·18	18·0	92·44
Au and Cu	1·64	65·36	18·1	92·82

All hard drawn; the amount of gold was determined.

Gold-Silver Series.

	Au			
Au_{34} Ag	98·81	59·09	25·1	73·25
Au_{56} Ag	98·23	53·24	25·7	73·41
Au_{36} Ag	97·27	48·86	25·9	73·67
Au_{16} Ag	94·07	38·12	26·4	74·54
Au_8 Ag	88·80	28·58	26·6	75·96
Au_6 Ag	85·61	24·99	21·5	76·83
Au_4 Ag	79·86	20·91	21·0	78·38
Au_2 Ag	66·47	16·20	20·2	82·01
Au Ag	49·78	14·59	22·2	86·52
Au Ag_2	33·14	16·30	19·9	91·03
Au Ag_4	19·86	20·94	21·2	94·62
Au Ag_6	14·18	25·29	19·9	96·16
Au Ag_8	11·02	29·87	19·5	97·02
Au Ag_{16}	5·84	41·19	20·5	98·42
Au Ag_{36}	2·68	56·54	23·8	99·27
Au Ag_{56}	1·74	60·63	21·9	99·58
Au Ag_{34}	1·17	73·85	22·1	99·68

All hard drawn, not analysed.

TABLE VI. (continued.)

Copper-Silver Series.

Alloy.	Volume per cent.	Mean of		Calculated conducting power from the volume.
		Conducting power.	Temperature.	
	Cu		°	
Cu and Ag.....	98·96	86·91	20·7	93·23
Cu and Ag.....	97·94	79·38	19·7	93·30
Cu and Ag.....	94·84	75·64	20·0	93·51
Cu and Ag.....	89·83	69·92	21·1	93·86
Cu and Ag.....	78·33	67·82	18·8	94·64
Cu and Ag.....	67·45	67·90	19·0	95·38
Cu and Ag.....	63·29	68·16	22·2	95·67
Cu and Ag.....	45·37	67·43	19·0	96·89
Cu and Ag.....	38·87	64·94	19·6	97·34
Cu and Ag.....	28·21	63·71	17·2	98·07
Cu and Ag.....	17·84	63·71	17·0	98·74
Cu and Ag.....	13·15	67·44	17·5	99·10
Cu and Ag.....	6·12	74·48	16·8	99·58
Cu and Ag.....	3·23	78·23	17·1	99·78
Cu and Ag.....	2·01	83·87	17·0	99·86

All hard drawn, and the silver determined.

Of the bismuth-gold alloys very few could be determined, as bismuth makes gold exceedingly brittle. Gold could not be drawn with 0·25 per cent. of bismuth. With silver-bismuth, however, better results were obtained. The bismuth-antimony alloys were determined, but as no concordant results were obtained, they will not be given; the curve, however, appeared to be similar to those of this class.

On looking at the gold-silver alloys, we find that

Au Ag conducts 14·59;
Au_2 Ag and Ag_2 Au conduct respectively 16·20 and 16·30;
Au_4 Ag and Ag_4 Au conduct respectively 20·91 and 20·94;
Au_6 Ag and Ag_6 Au conduct respectively 24·99 and 25·29;

and from these points the difference becomes greater as we approach the pure metals. But as 1 equivalent of gold $=\frac{197}{19\cdot265}=10\cdot226$ volumes, and 1 equivalent of silver $=\frac{108}{10\cdot468}=10\cdot317$ volumes, we may regard the alloy Au Ag as being composed of 1 volume of gold+1 volume of silver; and within the above limits we may add to the alloy Au Ag equal amounts of gold or silver and obtain the same conducting power, showing that gold and silver within these limits, when alloyed with one another, have the same conducting power. The same remarks hold good for some gold and copper alloys.

The curves of the alloys of this class show that there is a rapid decrement on both sides, of which I shall speak shortly.

5. *General Conclusions.*

The question now arises, What are alloys? Are they chemical combinations, or a solution of one metal in another, or mechanical mixtures? And to what is the rapid decrement in the conducting power in many cases due?

To the first of these questions I think we may answer, that most alloys are merely a solution of the one metal in the other; that only in a few cases we may assume chemical combinations, for example, in some of the gold-tin and gold-lead alloys; and we may regard as mechanical mixtures some of the silver-copper and bismuth-zinc alloys. The reasons of the foregoing assumptions are the following:—

1. That if we had to deal with chemical combinations, we should not find in the conducting power of alloys that regularity in the curves which certainly exists; for on looking at those belonging to the different classes, we see at a glance that each class of alloys has a curve of a distinct and separate form. Thus for the first, we have nearly a straight line; for the second, the conducting power always decreases rapidly on the side of the metal belonging to Class B, and then turning, goes almost in a straight line to the side of the metal belonging to Class A. For the third group, we find a rapid decrement on both sides of the curve, and the turning-points united by almost a straight line.

If we now examine the part of the curve where the rapid decrement takes place, we find that in the lead and tin alloys it generally requires twice as much of the former as it does of the latter to reduce a metal belonging to Class B. to a certain conducting power; for instance, to reduce that of silver to 67, it would require 0·9 vol. per cent. of lead, or about 0·5 vol. per cent. of tin; to reduce it to 47·6, there would be required 1·4 vol. per cent. of lead, or about 0·7 vol. per cent. of tin*. Again, to reduce bismuth to 0·261, there is required 1·4 vol. per cent. of lead, or 0·62 vol per cent. of tin; and to reduce it to the minimum point of the curve, which is, when alloyed with lead, 0·255, and 0·245 when alloyed with tin, it requires 1·76 vol. per cent. of lead and 0·85 vol. per cent. of tin.

2. We cannot explain the reason of the decrement of the conducting powers by assuming that the turning-points of the curves are chemical combinations, for it is not at all probable that there are such as contain only 0·6 per cent. of tin and 99·4 per cent. of bismuth; or 2 per cent. of lead and 98 per cent. of bismuth; or 2·6 per cent. of tin and 9·74 per cent. of silver, &c.

3. That the alloys, at these turning-points, have their calculated specific gravities†.

On Plate V. we find the curves of the alloys belonging to the third class: now here we might be inclined to think that we had to do with chemical combinations. But if we consider, taking the gold-silver curve as a type, that the conducting power of silver is greatly reduced by small per-centages of any metal, and that the same may be said of gold, and if we suppose that this decrement has taken place, and join the two turning-points to which the metals have been reduced, we shall have the gold-silver curve. Take,

* These values were read off from the curves.

† See the specific gravities of lead-bismuth and tin-bismuth alloys in this volume, pp. 162, 165, 166.

for instance, the gold-tin and the silver-tin curves, and connect the two turning-points, and we shall find that the curve so made is exactly similar to that of the gold-silver. Again, look at that of the silver-bismuth, and compare it in the same manner with the tin-silver and tin-bismuth curves, and we obtain similar results.

The gold-bismuth and silver-bismuth curves are exactly similar; the alloys of gold and bismuth conducting less than those of silver and bismuth, as would be expected, as silver is a better conductor than gold.

From the similarity of the curves of alloys, where we may assume, from their chemical behaviour, that we have only a solution of one metal in another, we may always draw approximatively the curve of the alloys of any two metals, if we know to which class they belong. Thus before a single copper-gold alloy had been determined, the curve was almost correctly drawn, and agreed with that which was afterwards found by experiment.

That some alloys are chemical combinations may be deduced from the following facts:—

1. At the turning-points of the curve we generally find the alloys contract or expand.
2. There is no regular form of curve (see those of gold-tin, gold-lead, and silver-copper), so that it cannot be *à priori* even approximatively represented.
3. At the turning-points the alloys contain large per-centages of each metal.
4. At the turning-points of the curves the alloys are different from each other in appearance (crystalline form, &c.).

Now let us for a moment examine the gold-tin curve, it being the only nearly complete one of this class, and starting from the tin side of it, we find a slow decrement in the conducting power to the alloy Sn_4Au; then a slow increment to Sn_2Au, and from this point a slow decrement to $SnAu_2$. For reasons before given, no alloys could be determined between $SnAu_2$ and that containing 2·7 per cent. of tin, from which point the curve goes in a straight line to pure gold. Starting again from the tin side of the curve, we may regard the alloys down to Sn_4Au as a solution of a chemical combination in a metal; from Sn_4Au to Sn_2Au, and from Sn_2Au to $SnAu_2$, as a solution of two chemical combinations in each other, as all of these points are connected with each other by straight lines; and from $SnAu_2$ to the alloy containing 2·7 per cent. of tin, as a solution of a chemical combination in an alloy, and from this point to pure gold as a solution of a small quantity of tin in gold.

Now these turning-points contain, first, Sn_4Au, 60 per cent.; second, Sn_2Au, 37 per cent.; and third, $SnAu_2$, 13 per cent. of tin, which may very well be considered to be chemical combinations. On looking at their specific gravities, we find that Sn_4Au has almost its calculated one, whereas Sn_2Au expands, and $SnAu_2$ contracts more than any other of the gold-tin alloys experimented with.

In their general appearance we see that $SnAu_2$ and Sn_2Au are not at all crystalline, and have a very glassy fracture; but Sn_4Au is exceedingly crystalline, and always shows, on being broken, the cleavage plane of a crystal from one end of the piece to the other.

For the above reasons I think there can be no doubt that the irregularity of the gold-tin curve is due to chemical combination, and that the same may be said of the gold-lead curve.

That some alloys are mechanical mixtures, we know from facts determined by other experimenters; thus, when we fuse 17·73 parts of bismuth and 16·12 parts of zinc together, we find two layers, the upper one consisting of 13·40 parts of zinc, and the lower one 19·40 parts of bismuth alloyed with traces of zinc*; now had we stirred the two metals well together, and cooled rapidly the alloy so obtained, it might be considered as a mechanical mixture.

Again, according to Levol†, if we fuse silver and copper together, and allow the alloy to remain quietly in the fused state, we find, on analysing the mass, that different parts contain different per-centages of metal: he found this to be the case with all alloys, excepting that containing 28·11 per cent. of copper, which corresponds to the formula $Ag_3 Cu_4$.

Levol regards all alloys of silver and copper as mixtures of $Ag_3 Cu_4$, and either silver or copper; if this were the case, we should have expected to find from that point to pure silver or copper, straight lines; but on examining that curve, starting from the copper side of it, we first see that a rapid decrement takes place, caused by the copper being alloyed with a small quantity of silver. From that alloy containing 90 vols. per cent. to that of 35 vols. per cent. of copper, we have a straight line, and we may regard the intermediate alloys as mixtures or solutions of these two alloys; from the alloy containing 35 vols. per cent. to that with 28 vols. per cent. of copper, we may have a mixture or solution of those alloys: now this last point is the minimum point of the curve, and corresponds almost to Levol's $Ag_3 Cu_4$, being an alloy containing 25 per cent. by weight of copper. This, as well as the other lowest points of the curves, must not be considered as actually the lowest, but only as the lowest point found; for in this case we should expect that the alloy containing 28 per cent. of copper would be lower; and from this point to pure silver the alloys may be mixtures, or perhaps solutions of that alloy and silver containing a small quantity of copper. Now it would appear as if at about the point which represents the alloy containing 35 vols. per cent. of copper, there was also one of constant composition, otherwise we should have expected a straight line from the alloy containing 28 vols. per cent. to that containing 90 vols. per cent. of copper.

Of course, from this one curve, we can hardly deduce any conclusions, as we have in all probability to deal with mixtures of chemical compounds, with solutions of the one metal in the other, &c. It only shows that, by the determination of the conducting powers of the alloys, we are able to tell where these are constant or chemical combinations; and when the curves are irregular, we may safely conclude that we have to do with chemical combinations or mechanical mixtures.

That the first group of alloys, their curves being nearly straight lines, are not mix-

* Fournet, Ann. de Chim. et de Phys., vol. liv. p. 247.

† Journ. de Pharm., vol. xvii. p. 111.

tures but solutions of one metal in the other, may be deduced from the fact of their fusing-points being generally lower than the mean of that of the volumes taken.

Secondly. To what is the rapid decrement of the conducting power due?

The only answer which I can at present give to this question, is that most of the other physical properties of the metal are altered in a like manner; for on looking at the alloys made with the metals of Class A. with one another, we see that most of their other physical properties are not at all altered; for amongst them, for instance, we find no brittle ones; they appear, in fact, to take an equal share of the properties of the metals composing them. But now let us examine the alloys of the second class, and we immediately discover great differences; alloy gold, the most ductile of all metals, with small per-centages of tin, lead, or zinc, and it becomes as brittle as glass. Again, alloy silver with small per-centages of the above metals, and its properties are much altered. Silver, which, when pure, is one of the easiest metals to draw, when alloyed with more than 3 per cent. of tin and 2 per cent. of lead, becomes so brittle, and its tenacity so much impaired, that it cannot be drawn. I do not mean to say it is impossible to do so, but it was tried several times without success. On the other hand, we do not find any marked differences in the ductility, hardness, &c. of tin or lead when alloyed with silver; we may add 10, nay even 20 per cent. of silver to them, and they remain ductile, and may be pressed into wire without any trouble. Of course, with lead and tin alloyed with small quantities of gold, the case is somewhat different, as we have here chemical combinations coming into play; nevertheless, we may add to them 5 per cent. of gold without altering their ductility, &c. to any great extent. Bismuth alloyed with lead or tin becomes more brittle, and in wire its tenacity is impaired; but tin and lead alloyed with large per-centages of bismuth, always retain a considerable amount of ductility, &c.

Again, take the alloys of the third class. Although amongst the gold-silver and the gold-copper alloys we find no brittle ones, yet we know how hard gold, silver, and copper become when we alloy them with small quantities of other metals, and that they lose more in proportion of their ductility, &c., by the addition of small than of large quantities of strange metal.

From these facts, we need not be surprised at the rapid decrement of the conducting powers of the metals belonging to Class B, when alloyed with any other metal; for when we find most of their other physical properties more or less greatly altered by traces of foreign metals, might we not also have expected this result? For where we see no marked change in most of the other physical properties of alloys, as in the first class and in the second, on the one side of the curve, there we have nearly their calculated conducting powers.

It would be very interesting to determine quantitatively some of the other physical properties of the alloys, to see whether in them these properties will decrease in the same marked manner as the conducting powers, when a metal belonging to Class B. is alloyed with any other metal. I intend therefore to commence, especially with this

view, with the conducting power for heat, in order to see if the classification of the metals and alloys given in this paper will hold good for any of the other physical properties, as well as in the hope of finding out the cause of the behaviour of the metals of Class B. when alloyed with traces of any other. On looking at the specific gravity of alloys*, we find that they cannot be classified as above, but in all probability the above classification will hold good for their tenacity, hardness, conducting power for heat, &c.

APPENDIX.

On the Electric Conducting Power of Pure Gold.

The values given for the conducting power of pure gold, in my paper "On the Electric Conducting Power of the Metals†," is not quite correct, as the gold from some cause cannot have been chemically pure; although prepared with the greatest care by Dr. MEYBOOM, yet the wire-drawer in all probability fused it in a crucible which had been previously used; and as only 3 to 4 grms. were purified, a very small amount of impurity would account for the difference which I have lately found. At the time the values appeared very low, compared with those of other experimenters, but it was then thought that the higher ones were due to traces of silver. Experiments, however, have proved, on the contrary, that most of the gold-silver, gold-copper, &c. alloys conduct electricity worse than pure gold; and that, in fact, only those which contain less than 2 per cent. gold in gold-silver alloys, and about 3 per cent. gold in gold-copper alloys, conduct better than pure gold.

Thus chemically-pure gold, prepared by dissolving gold from the refiners in nitrohydrochloric acid, precipitating with algaroth powder, washing alternately with nitric and hydrochloric acids, redissolving in nitrohydrochloric acid, precipitating by sulphurous acid, washing alternately with nitric and hydrochloric acids, and fusing in a muffle with nitrate of potash, gave, compared with a hard drawn silver wire =100 at 0°C.,

I.	II.	III.	Mean.
73·57 at 19°·0	72·10 at 19°·1	72·37 at 19°·8	72·68 at 19°·3.

Another specimen, prepared in the same manner, gave

I.	II.	III.	Mean.
72·80 at 23°·0	73·42 at 23°·8	73·02 at 23°·1	73·08 at 23°·3.

A third specimen, prepared by dissolving gold containing silver in nitrohydrochloric acid, evaporating to dryness with excess of hydrochloric acid, dissolving in about 500 times its weight of water‡ and precipitating with protosulphate of iron, washing out all

* See specific gravities of tin-bismuth and lead-bismuth alloys in this volume, pp. 162, 165, 166.

† Philosophical Transactions, 1858.

‡ It is of the greatest importance, in purifying gold containing silver by this method, that the solution should be made very dilute, so that the chloride of silver dissolved in the chloride of gold may be precipitated before the addition of the protosulphate of iron; otherwise the chloride of silver would fall with the

the iron with boiling hydrochloric acid, and fusing with nitrate of potash and a little borax, gave—

I.	II.	Mean.
73·63 at 13°·5	72·90 at 14°·2	73·27 at 13°·8.

A fourth specimen, prepared exactly as the third, gave—

I.	II.	Mean.
74·20 at 14°·8	73·78 at 15°·5	73·99 at 15°·1.

The so-called proof-gold of the refiners gave—

I.	II.	III.
65·57 at 23°·1	64·25 at 23°·1	65·92 at 23°·1 *.

In conclusion, I give a list of the determinations of gold as found by other experimenters, silver taken =100:—

Riess†.	Lenz†.	Ed. Becquerel‡.	Harris†.	H. Davy†.	Christie†.
59	58·5	64·9	66·6	67	73

Matthiessen.
55·19 and 73·26 at 17°·8.

On looking over these values, we find that all, except that of Christie, are too low, and the gold-silver alloys which correspond to these numbers are the alloys which contain

99·4 per cent. gold and 0·6 per cent. silver, conducting 59,
99·7 per cent. gold and 0·3 per cent. silver, conducting 66.

Now the proof-gold of the refiners often contains as much as 0·5 per cent. silver, and the value 66 found for it would be that of the alloy 99·7 per cent. gold and 0·3 per cent. silver.

Of course the value given in my paper "On the Thermo-electric Series," for the thermo-electric number of pure gold, cannot be correct, as I used the same gold for those determinations and for those of the conducting power.

I am much indebted to Dr. M. Holzmann for the excellent manner in which he has carried out the greater part of the foregoing determinations.

gold, and be reduced during the process of fusion. The following experiments prove this to be the case; they were carried out in every respect in the same manner, and with the same care as those above, the only difference being in the concentration of the solution.

Thus gold containing silver was dissolved in nitrohydrochloric acid, evaporated to dryness with excess of hydrochloric acid, dissolved in a small quantity of water and precipitated by a concentrated solution of protosulphate of iron, washed alternately by boiling nitric and hydrochloric acids, redissolved in nitrohydrochloric acid, reprecipitated by protosulphate of iron, washed alternately with nitric and hydrochloric acids and fused with nitrate of potash, and then gave

66·57 at 22°·0.

Another specimen, prepared by precipitating a concentrated solution of gold by protosulphate of iron, washing, &c., redissolving and precipitating by sulphurous acid, washing, &c., gave—

I. 67·87 at 22°·3. II. 67·78 at 22°·3.

* For all the above determinations, hard-drawn wires were used.

† Gmelin, vol. i. p. 289. ‡ Ann. de Chim. et de Phys. iii. 17, 242.

XI. *On the Specific Gravity of Alloys.* By A. Matthiessen, *Ph.D.*

Communicated by Professor Wheatstone.

Received November 17,—Read December 22, 1859.

Before commencing a research on the law of the conducting power for electricity of alloys, it was considered necessary to determine their specific gravities; to ascertain whether they expand or contract, so as to be able to account for differences which might be obtained in their conducting powers.

The metals used for the alloys were those which were easily obtained in a pure state in large quantities, and were purified as follows:—

1. *Antimony.*—By Liebig's process.

2. *Tin.*—Commercial metal dissolved in nitric acid, and the binoxide reduced by charcoal.

3. *Cadmium.*—Commercial metal dissolved in hydrochloric acid and precipitated by sulphuretted hydrogen; the sulphide dissolved in hydrochloric acid and precipitated by carbonate of soda; the carbonate heated, a part of the oxide reduced by hydrogen, and the rest distilled with charcoal.

4. *Bismuth.*—Commercial metal dissolved in nitric acid, precipitated by water and reduced by charcoal.

5. *Silver.*—Reduced from the pure chloride by fusion with carbonate of soda. The greater part of the silver used for making the alloys was procured in a state of purity from Messrs. Johnson and Matthey.

6. *Lead.*—Commercial acetate recrystallized three times and heated.

7. *Mercury.*—Commercial metal treated with nitric acid, and allowed to stand with it about a month, being at intervals well-shaken.

8. *Gold.*—Prepared by precipitating chloride of gold by algaroth powder, &c., and also by precipitation of the chloride of gold by protosulphate of iron*, &c. Some of the gold employed was procured pure from Messrs. Johnson and Matthey.

The quantity of each alloy made was about 20 grms.; the two metals were weighed out accurately in proper proportions, and fused together in a porcelain crucible; a jet of gas being allowed to play in the same from above to prevent the oxidation of the metals. The alloys were cast in a wooden mould, a porcelain slab (previously blackened by holding it over a gas flame to prevent the adhering of the metal) forming the bottom. They were always re-fused and re-cast, at least three times, before the first determination was made, then re-fused before they were determined a second time, and again before

* See Appendix at the end of my paper "On the Electric Conducting Power of Alloys," in this volume, p. 175.

the third determination; often being re-cast several times, as the castings did not always succeed. To prevent as much as possible the formation of internal cavities from crystallization, the alloys were cast very thin, the thickness of the casting being in most cases about 3 to 4 millims.

The method employed for taking the specific gravities, was that of hanging the alloys by a very fine platinum wire in distilled water, which had been boiled to free it from air, and allowed to cool *in vacuo*. This method gave better results than that of weighing the metal or alloy in a bottle filled with water, on account of the difficulty of perfectly drying the bottle when full, and obtaining the same weight twice following.

The amalgams which were liquid, and those not sufficiently hard to hang by the platinum wire, were weighed in a glass tube to which a platinum wire was soldered.

The weight of the tube alone in air and water was determined at the temperature at which the experiments were made, and therefore, in calculating the specific gravities, these values had only to be subtracted from those found.

The balance used was one of LIEBIECH'S, which turns to the 0·1 mgr. when loaded with 100 grms. in each pan; and when the alloy was weighed in water, it turned to the 0·2 mgr. The air adhering to the alloy, when weighed in water, was removed by a soft brush, the alloy being brushed until its weight became constant.

In calculating the specific gravities, the weight of the water displaced was corrected for the temperature, so that the unit is in all cases distilled water at 0° C. A similar correction could not be made for the temperature of the alloys, as their coefficients of expansion are not known. All the weighings were reduced to a vacuum, and a correction was made for that part of the platinum wire which dipped in the water. The length of wire dipping in was about 60 millims., which weighed 8 mgrs.; these would lose in water about 0·35 mgr. Supposing, as is really the case, that sometimes 10 millims. more or less dipped in, the error made would be about 0·06 mgr.; but as the 0·3 mgr. only make an error, if not brought into calculation, in most cases of about 0·001 per cent. of the specific gravity found, the error made in this way may be overlooked.

The equivalents used for calculating the quantities of metal required for the alloys were—

Antimony*	122·3	Silver	108
Tin	58	Lead	103·7
Cadmium	56	Mercury	100
Bismuth	208	Gold	197

Table I. gives the specific gravities of the pure metals employed, and the temperature (T.) in the Centigrade scale: the values given are the results of three consecutive determinations. On account of the number of alloys experimented with, it was considered as well, in order to save space, only to give the mean of the three determinations; and

* DEXTER, POGGENDORFF'S 'Annalen,' vol. c. p. 563. This is the latest determination, and the one adopted by BUNSEN in his recent paper. LIEBIG'S 'Annalen,' vol. cvi. p. 1.

where they did not agree amongst themselves to 0·1 per cent. of the value, a + will be placed by the alloy, and the value there given is the mean of a number of experiments (generally six or more)*.

TABLE I.

Specific gravity found.

Metal.	1st Determination.	T.	2nd Determination re-fused.	T.	3rd Determination re-fused.	T.	Mean of		Determined by
							Spec. grav.	T.	
Antimony ...	6·715	13°·6	6·713	14°·4	6·710	15°·0	6·713	14°·3	A. Matthiessen.
Tin	7·293	11·5	7·295	12·8	7·294	14·0	7·294	12·8	A. Matthiessen.
Cadmium.....	8·655	10·0	8·657	10·2	8·654	11·2	8·655	10·5	A. Matthiessen.
Bismuth	9·823	12·0	9·824	12·4	9·823	12·4	9·823	12·3	Dr. M. Holzmann.
Silver†.....	.....	...	.....	...	.....	...	10·468	13·2	Dr. M. Holzmann.
Lead	11·374	13·0	11·380	16·5	11·376	11·0	11·376	13·5	Dr. M. Holzmann.
Mercury	13·575	14·0	13·569	14·7	13·574	14·8	13·573	14·5	Dr. M. Holzmann.
Gold	19·261	10·0	19·269	15·5	19·264	12·8	19·265	12·8	A. Matthiessen.

Table II. gives the mean of the three determinations made with the alloys, the mean of the temperatures (T.), and the specific gravity calculated from the first of the following formulæ:—

$$S=\frac{A+A_1}{V+V_1}=\left(\frac{Vs+V_1s_1}{V+V_1}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

$$S=\frac{ns+n_1s_1}{n+n_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

$$S=\frac{As+A_1s_1}{A+A_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

where

S = the specific gravity of the alloy,
V and V_1 = the volumes of the metals, taking
n and n_1 = the numbers of the equivalents of the metals, and
A and A_1 = their respective weights.
s and s_1 = their specific gravities.

* Those alloys which are underlined have been made twice, as it was supposed these must have an error in the weighing out of the metals, as they do not agree with the calculated values. The values, however, were found to be correct.

† No concordant results could be obtained with this metal. Experiments were made with it after having been fused under borax, chloride of sodium, charcoal, in hydrogen. The above value is the mean of a number of determinations which varied between 10·424 and 10·511.

Some specimens of not quite pure silver were lent me by Mr. PH. WORSLEY, who prepared them as follows:—

The silver was made as hot as possible, and well-stirred with a stick of charcoal before pouring. The mould was a steel one, forming a bar of about 25 millims. square and about 300 millims. high. The bar weighed about 2½ kilogrammes. The top of it, when cold, showed a funnel-shaped depression, and the soundest part of it was about two-thirds down, and from this different pieces were cut, which gave very good results. The values obtained were 10·504, 16°·7; 10·505, 17°·2; 10·502, 19°·2. A second bar gave similar numbers; they were 10·500, 24°·5; 10·496, 24°·8; 10·492, 25°·0.

The specific gravity of an alloy is calculated from the above formulæ, under the supposition that the specific gravity of the metals employed take part of that of the alloy in the ratio of their relative volumes (1.), equivalents (2.), or weights (3.). Of these formulæ only the first is for all cases correct, supposing the alloy neither contracts nor expands; the second only when the volumes and equivalents of the metals employed are in the same ratio with each other, as in the case of gold, silver, &c.; and the third only when the specific gravities of the two metals are equal. The two last methods of calculation are here mentioned, as several chemists have calculated their results from these formulæ.

TABLE II.

Antimony-Tin Series (determined by Mr. C. LONG).

Alloy.	Mean of		Calculated specific gravity, from volume.	Ratio of volumes, $\frac{V+V_1}{v}$ *
	Specific gravity found.	T.		
Sb_6Sn	6·739	16·2	6·752	1·0019
Sb_4Sn	6·747	13·4	6·770	1·0034
Sb_2Sn	6·781	13·5	6·817	1·0053
$SbSn$	6·844	13·8	6·889	1·0066
$SbSn_2$	6·929	15·8	6·984	1·0079
$SbSn_4$	7·023	15·8	7·082	1·0084
$SbSn_6$	7·100	10·6	7·133	1·0046
$SbSn_{10}$+	7·140	19·0	7·186	1·0065
$SbSn_{50}$	7·208	18·5	7·234	1·0036
$SbSn_{80}$	7·276	19·4	7·262	0·9981
$SbSn_{100}$	7·279	20·0	7·281	1·0003
$SbSn_{200}$	7·284	20·2	7·287	1·0004

Antimony-Bismuth Series (determined by Dr. M. HOLZMANN).

Sb_2Bi	7·864	9·4	7·856	0·9989
$SbBi$	8·392	11·0	8·385	0·9991
$SbBi_2$	8·886	14·0	8·888	1·0002
$SbBi_4$	9·277	12·1	9·272	0·9995
$SbBi_6$	9·435	9·4	9·433	0·9998

Antimony-Lead Series (determined by A. MATTHIESSEN).

$SbPb$	8·201	13·7	8·268	1·0082
$SbPb_2$	8·989	11·7	9·945	1·0062
$SbPb_4$	9·811	14·3	9·822	1·0011
$SbPb_6$	10·144	15·4	10·211	1·0066
$SbPb_{10}$	10·586	19·3	10·599	1·0012
$SbPb_{20}$+	10·930	19·9	10·952	1·0020
$SbPb_{50}$	11·194	20·5	11·196	1·0002

* Where v = volume of the alloy found, and $V+V_1$ = volumes of the metals composing it.

TABLE II. (continued.)

Tin-Cadmium Series (determined by A. MATTHIESSEN).

Alloy.	Mean of		Calculated specific gravity, from volume.	Ratio of volumes, $\frac{V+V_1}{v}$.
	Specific gravity found.	T.		
Sn_6 Cd	7·434	12°·7	7·456	1·0029
Sn_4 Cd	7·489	15·0	7·524	1·0047
Sn_2 Cd	7·690	12·9	7·687	0·9996
Sn Cd	7·904	13·2	7·905	0·9999
Sn Cd_2	8·139	11·1	8·137	0·9998
Sn Cd_4	8·336	14·5	8·335	0·9999
Sn Cd_6	8·432	15·0	8·424	0·9990

Tin-Bismuth Series (determined by Mr. M. CARTY).

Sn_{44} Bi	7·438	19·9	7·438	1·0000
Sn_8 Bi	7·943	20·0	7·925	0·9977
Sn_6 Bi	8·112	14·2	8·071	0·9949
Sn_4 Bi	8·339	13·9	8·305	0·9959
Sn_2 Bi	8·772	12·6	8·738	0·9961
Sn Bi	9·178	15·9	9·132	0·9950
Sn Bi_2	9·435	15·0	9·423	0·9987
Sn Bi_4	9·614	12·7	9·606	0·9991
Sn Bi_6	9·675	15·2	9·674	0·9999
Sn Bi_{10}	9·737	19·8	9·731	0·9994
Sn Bi_{20}	9·774	23·0	9·792	1·0019
Sn Bi_{44}	9·803	22·8	9·801	0·9998
Sn Bi_{80}	9·811	19·0	9·807	0·9996
Sn Bi_{90}	9·814	19·5	9·812	0·9998
Sn Bi_{200}	9·815	18·1	9·818	1·0003

Tin-Silver Series (determined by Dr. M. HOLZMANN).

Sn_{26} Ag+	7·421	18·6	7·404	0·9977
Sn_{10} Ag	7·551	18·8	7·507	0·9941
Sn_{13} Ag+	7·666	18·4	7·603	0·9918
Sn_6 Ag+	7·963	19·3	7·858	0·9868
Sn_4 Ag+	8·223	16·3	8·071	0·9815
Sn_2 Ag	8·828	13·8	8·543	0·9677
Sn Ag	9·507	12·9	9·086	0·9558
Sn Ag_2	9·953	14·8	9·585	0·9630

Tin-Lead Series (determined by Mr. C. LONG).

Sn_6 Pb	7·927	15·2	7·948	1·0027
Sn_4 Pb	8·188	16·0	8·203	1·0018
Sn_2 Pb	8·779	17·2	8·781	1·0002
Sn Pb	9·460	15·5	9·474	1·0015
Sn Pb_2	10·080	14·8	10·136	1·0055
Sn Pb_4	10·590	14·3	10·645	1·0052
Sn Pb_6	10·815	15·6	10·857	1·0039

Tin-Mercury Series (determined by Dr. M. HOLZMANN).

Sn_2 Hg	9·362	9·9	9·282	0·9914
Sn Hg	10·369	14·2	10·313	0·9946
Sn Hg_2	11·456	11·3	11·373	0·9927

TABLE II. (continued.)

Tin-Gold Series (determined by Dr. M. HOLZMANN).

Alloy.	Mean of		Calculated specific gravity, from volume.	Ratio of volumes, $\frac{V+V_1}{v}$
	Specific gravity found.	T.		
Sn_{100} Au	7·441	22°·9	7·446	1·0007
Sn_{20} Au	7·801	22·8	7·786	0·981
Sn_{18} Au	8·118	22·4	8·092	0·9968
Sn_{12} Au	8·470	23·1	8·452	0·9979
Sn_8 Au	8·931	25·6	8·951	1·0023
Sn_6 Au	9·405	23·7	9·407	1·0002
Sn_5 Au	9·715	22·4	9·743	1·0029
Sn_4 Au	10·168	23·7	10·206	1·0037
Sn_3 Au	10·794	23·6	10·885	1·0084
Sn_2 Au	11·833	14·6	11·978	1·0022
Sn Au	14·244	14·2	14·028	0·9848
Sn Au_2	16·367	15·4	15·913	0·9722

Cadmium-Bismuth Series (determined by A. MATTHIESSEN).

Cd_8 Bi	9·079	13·1	9·067	0·9987
Cd_4 Bi	9·195	15·5	9·181	0·9985
Cd_2 Bi	9·388	15·0	9·380	0·9991
Cd Bi	9·554	13·4	9·550	0·9996
Cd Bi_2	9·669	14·8	9·668	0·9999
Cd Bi_4	9·737	14·7	9·740	1·0003
Cd Bi_6	9·766	15·4	9·766	1·0000

Cadmium-Lead Series (determined by Dr. M. HOLZMANN).

Cd_8 Pb	9·160	13·7	9·173	1·0014
Cd_4 Pb	9·353	12·0	9·364	1·0012
Cd_2 Pb	9·755	14·7	9·780	1·0026
Cd Pb	10·246	11·7	10·246	1·0000
Cd Pb_2	10·656	13·4	10·663	1·0006
Cd Pb_4	10·950	9·2	10·966	1·0015
Cd Pb_6	11·044	14·8	11·088	1·0039

Bismuth-Silver Series (determined by Dr. M. HOLZMANN).

Bi_{200} Ag	9·802	23·5	9·825	1·0023
Bi_{50} Ag	9·813	23·6	9·829	1·0016
Bi_{24} Ag	9·820	23·3	9·836	1·0016
Bi_{12} Ag	9·836	21·8	9·848	1·0012
Bi_6 Ag	9·859	21·0	9·871	1·0012
Bi_4 Ag	9·899	15·2	9·893	0·9994
Bi_2 Ag	9·966	14·9	9·949	0·9983
Bi Ag	10·068	15·6	10·034	0·9966
Bi Ag_2	10·197	13·2	10·141	0·9945
Bi Ag_4	10·323	15·1	10·249	0·9928

TABLE II. (continued.)

Bismuth-Lead Series (determined by Mr. M. CARTY).

Alloy.	Mean of		Calculated specific gravity, from volume.	Ratio of volumes, $\frac{V+V_1}{v}$.
	Specific gravity found.	T.		
		°		
$Bi_{20}Pb$	9·844	21·7	9·845	1·0001
$Bi_{24}Pb$	9·845	21·6	9·850	1·0005
$Bi_{30}Pb$	9·850	21·3	9·856	1·0006
$Bi_{12}Pb$	9·887	20·6	9·877	0·9990
$Bi_{10}Pb$	9·893	19·5	9·887	0·9994
Bi_8Pb	9·934	21·1	9·902	0·9968
Bi_6Pb	9·973	15·0	9·927	0·9953
Bi_4Pb	10·048	10·7	9·974	0·9927
Bi_2Pb	10·235	12·5	10·098	0·9866
$BiPb$	10·538	14·0	10·290	0·9765
$BiPb_2$	10·956	14·9	10·541	0·9621
$BiPb_4$	11·141	12·7	10·805	0·9698
$BiPb_6$	11·161	14·8	10·942	0·9803
$BiPb_8$	11·188	20·8	11·026	0·9855
$BiPb_{10}$	11·196	20·2	11·083	0·9899
$BiPb_{24}$	11·280	22·5	11·238	0·9963
$BiPb_{100}$	11·331	23·0	11·340	1·0008

Bismuth-Gold Series (determined by Dr. M. HOLZMANN).

$Bi_{80}Au$	9·872	21·0	9·873	1·0001
$Bi_{40}Au$	9·942	21·2	9·935	0·9993
$Bi_{20}Au$	10·076	18·7	10·046	0·9970
Bi_8Au	10·452	21·4	10·360	0·9912
Bi_4Au	11·025	23·0	10·840	0·9833
Bi_2Au	12·067	16·0	11·659	0·9662
$BiAu$	13·403	16·5	12·898	0·9631
$BiAu_2$	14·844	16·0	14·462	0·9743

Silver-Lead Series (determined by A. MATTHIESSEN).

Ag_2Pb	10·800	13·5	10·746	0·9950
$AgPb$	10·925	13·8	10·894	0·9971
$AgPb_2$	11·054	12·5	11·048	0·9995
$AgPb_4$	11·144	18·2	11·175	1·0028
$AgPb_8$	11·196	21·0	11·263	1·0060
$AgPb_{20}$	11·285	22·2	11·327	1·0037
$AgPb_{50}$	11·334	20·6	11·355	1·0018

Silver-Gold Series (determined by A. MATTHIESSEN).

Ag_8Au	11·760	13·1	11·715	0·9961
Ag_4Au	12·257	14·7	12·215	0·9965
Ag_2Au	13·432	14·3	13·383	0·9963
$AgAu$	14·870	13·0	14·847	0·9984
$AgAu_2$	16·354	13·0	16·315	0·9976
$AgAu_4$	17·540	12·3	17·493	0·9973
$AgAu_8$	18·041	13·1	17·998	0·9976

TABLE II. (continued.)

Lead-Mercury Series (determined by A. MATTHIESSEN).

Alloy.	Mean of		Calculated specific gravity, from volume.	Ratio of volumes, $\frac{V+V_1}{v}$
	Specific gravity found.	T.		
Pb_2Hg	11·979	15°·9	12·008	1·0024
$PbHg$	12·484	15·7	12·358	0·9899
$PbHg_2$	12·815	15·5	12·734	0·9937

Lead-Gold Series (determined by A. MATTHIESSEN).

$Pb_{20}Au$	11·841	23·3	11·794	0·9961
$Pb_{10}Au$	12·274	19·4	12·171	0·9916
Pb_8Au	12·445	21·6	12·346	0·9920
Pb_6Au	12·737	21·3	12·618	0·9906
Pb_4Au	13·306	22·1	13·103	0·9840
Pb_2Au	14·466	14·3	14·210	0·9823
$PbAu$	15·603	14·5	15·546	0·9963
$PbAu_2$	17·013	14·3	16·832	0·9894

From Table II., which gives in the fourth column the ratio of the sum of the volumes of the two metals to the volume of the alloy, it appears that the alloys of antimony are generally greater in volume than the aggregate of the constituent metals (expand), while those of bismuth, silver, gold, and mercury, generally are less (contract); and we find that the maximum expansion or contraction generally takes place about that point when the alloy contains equal volumes of each metal.

The gold-tin and gold-lead alloys are all very brittle, except those very rich in lead or tin:—$SnAu_2$ to Sn_2Au are not at all crystalline, and have a glassy fracture; Sn_4Au begins to show a crystalline structure, and has a crystalline fracture; Sn_8Au to $Sn_{100}Au$ are exceedingly crystalline; and Sn_2Au to $Sn_{12}Au$ all show a fracture like the cleavage plane of a crystal. The gold-lead alloys appear all to be crystalline, that is, their surface is very much so, but their fracture is glassy. The following alloys expand greatly on cooling, so much so, that the liquid metal breaks through the crust, forming large or small globules, viz. all those of bismuth-antimony, bismuth-gold, and bismuth-lead, which were experimented on; those of bismuth-tin, from $Bi_{210}Sn$ to Bi_2Sn, the rest of the series very slightly; and bismuth-lead, viz. $Bi_{30}Pb$ to Bi_4Pb (Bi_2Pb slightly), the rest apparently not at all. Of the bismuth-cadmium series, $BiCd_8$ and $BiCd_4$ expand very slightly, the rest not at all. No concordant results could be obtained with any zinc-tin or zinc-cadmium alloys, on account of their very crystalline structure.

In conclusion, my best thanks are due to Dr. M. HOLZMANN, Mr. C. LONG, and Mr. M. CARTY for their assistance in carrying out the foregoing determinations.

XII. The Bakerian Lecture.—*Experimental Researches to determine the Density of Steam at different Temperatures, and to determine the Law of Expansion of Superheated Steam.* By William Fairbairn, *Esq.*, *F.R.S.*, *and* Thomas Tate, *Esq.*

Received March 23,—Read May 10, 1860.

The object of these researches is to determine by direct experiment the law of the density and expansion of steam and other condensable vapours at all temperatures. Dumas determined with great accuracy the density of steam at 212°, but at this temperature only. Gay-Lussac and other physicists since his time have deduced the density of steam at different temperatures from a theoretical formula, which assumes that steam follows the same law of expansion and contraction as a perfectly elastic fluid.

The law which determines the relation between temperature, volume, and pressure, in the case of a perfect gas is expressed by the equation

$$\frac{VP}{V_1P_1}=\frac{\varepsilon+T}{\varepsilon+T_1}, \quad \ldots \quad (1.)$$

where V is the volume of the gas at P pressure and T temperature; V_1 the volume at P_1 pressure and T_1 temperature; ε=a constant, the value of which, according to Regnault's experiments, is for air 459. Now, assuming that steam follows the gaseous laws, we have, according to the experiments of Dumas, V_1=1669, the volume of steam raised from a unit of water at the temperature of 212°, and at the pressure of 14·7 lbs. per square inch. Making these substitutions in equation (1.), we get for the volume of steam from a unit of water at any other temperature T and pressure P,

$$V=1669\times 14{\cdot}7\,\frac{459+T}{671\times P}$$

$$=36{\cdot}5\,\frac{459+T}{P}. \quad \ldots \quad (2.)$$

From this well-known formula all the tables of the density of steam have hitherto been deduced, on which calculations of the duty of steam-engines have been founded.

Although experimentalists have for some time questioned the truth of this theoretical formula, yet up to the present time *no reliable direct experiments* have been made to test its truth. More recently, Dr. Joule and Professor Thomson announced as the result of the application of the dynamical theory of heat, that for temperatures above 212° Fahr. there would prove to be a considerable deviation from the gaseous laws in the case of steam. In 1855, Professor Rankine gave a theoretical formula for the density of steam confirmatory of Professor Thomson's views. About the same time, and without any knowledge of Professor Rankine's formula, Mr. Tate made some experiments with the

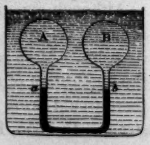
vapour of ether, which led him to conclude that at pressures somewhat above the atmospheric, the vapour of this substance does not follow the gaseous laws. Although these experiments were conducted on a scale too limited for deriving exact quantitative results, they enabled him to test the precision and delicacy of the *saturation-gauge*, which forms the leading feature of the method on which the following experiments were conducted. As yet, therefore, the results derived from the dynamical theory of heat require to be verified by direct experiments.

The general features of our method of ascertaining the density of steam consist in vaporizing a known weight of water in a large glass globe with a stem, of known capacity and devoid of air, and observing the exact temperature at which the whole of the water is just vaporized. Then, knowing the weight, volume, and temperature of the steam, its specific gravity may be calculated. In order to pursue this method with safety and with the requisite amount of accuracy, the following peculiarities of construction of the apparatus were adopted:—

First. In order to secure the thin globe from bursting, and at the same time to have it uniformly heated, it is placed in a strong closed copper steam-bath, having a thermometer and pressure-gauge attached, and a strong glass tube, closed at its exterior extremity, passing through a stuffing-box for receiving the stem of the globe. By this arrangement the glass globe is secured from bursting; for whatever may be the elasticity of the steam, the internal pressure in the globe is always exactly balanced by the external pressure in the steam-bath.

Second. When a given weight of water is vaporized in a closed vessel, devoid of air, the steam is said to be in a state of saturation so long as any portion of liquid remains in the vessel; but after all the water is vaporized, heat being still applied, the steam becomes superheated, or heated beyond the temperature just requisite for vaporizing all the water; by way of distinction, we shall call this point *the maximum temperature of saturation*. Now since we have to find *by observation* the temperature of the steam exactly at the point when the whole of the water is vaporized, the determination of this, with sufficient accuracy and delicacy, has hitherto formed the great practical difficulty attending experimental researches on the density of vapours. We have overcome this difficulty by using what may be called a *saturation gauge*, the form of which varies according to circumstances, but the principle on which it is constructed may be illustrated as follows:—

Fig. 1.



Imagine two globes, A, B, fig. 1, connected by a bent tube containing mercury and immersed in a large bath of liquid, to secure uniformity of temperature. Suppose these globes devoid of air, but containing weighed portions of water, say 20 grains in A and 30 in B. If heat be now applied to the liquid-bath so as to increase the temperature of the globes, this weighed portion of water will gradually pass into steam, and the elastic force in each globe will increase in a ratio corresponding with the temperature, but without in the least affecting the uniformity of level

of the mercury columns a and b, because the pressure on each side will be the same. But after the whole of the water in the globe A has been evaporated, this equality of pressure no longer exists, and the column a will rise. The pressure in B increases in the ratio for saturated steam, whilst that in A increases in the much smaller ratio of superheated steam, and hence the difference of level of the columns. The instant at which the columns begin to rise on one side and to fall on the other, is the point at which the whole of the water in A is converted into steam, and the temperature then noted is the maximum temperature of saturation. The following theoretical Table gives, approximately, the rise of the mercury column at several temperatures:—

lbs.	°	Increments of pressure for 1° Fahr. for expansion.	for vaporization.	Difference.
At 4 and	152	0·012	0·222	0·21
At 7 and	176	0·022	0·32	0·30
At 15 and	213	0·044	0·60	0·56
At 20 and	228	0·060	0·80	0·74
At 61 and	295	0·16	2·00	1·84
At 74 and	308	0·20	2·22	2·02

In Plate VII. fig. 1 is an elevation, fig. 2 a section, and fig. 3 a plan of the apparatus employed in these researches for pressures varying from 15 to 70 lbs. on the square inch, or from one to five atmospheres. A is the glass globe for the reception of the weighed portion of water, drawn out into a stem about 32 inches long. The average size of the globes was $5\frac{1}{4}$ inches in diameter, or 75 cubic inches capacity; the stems were about $\frac{3}{8}$ to $\frac{7}{16}$ inches bore. B B is the copper boiler or steam-bath in which the globe was heated uniformly throughout. The copper bath is prolonged by a strong glass tube, $o\,o$, $1\frac{1}{4}$ inch in diameter, and hermetically sealed at the bottom: this tube is fixed to the boiler by a stuffing-box, $s\,s$, its upper part being trumpet-mouthed to prevent its being forced down by pressure; the joint in the stuffing-box was made by a thick ring of vulcanized india-rubber, which, with the temperatures employed in this apparatus, answered its purpose perfectly. To heat this outer tube uniformly, which, from being exposed to pressure as well as temperature, was exceedingly liable to explode, an outer oil-bath, C C, was used, made of blown glass, 20 inches long, and resting in a sand-bath, $l\,l$. This bath was supported on the tripod $m\,m\,m$. The copper bath was heated by a spiral coil of jets of gas, E E, and the oil-bath by a large and powerful wire-gauze lamp, $h\,h$, protected from draughts by a simple ring of sheet iron, $k\,k$. The temperature thus obtained and distributed uniformly throughout the glass tube and steam-bath by convection, was measured by the thermometer u in the oil, and the thermometer t in the steam, exposed naked, and fixed by the stuffing-box v. Opposite to the thermometer, t, is the stopcock, p, by which the steam is, if necessary, blown off; and on the top of the boiler is a gauge, G, of the Schæffer construction, for roughly indicating the pressure in the boiler. The two mercury columns, the outer in the tube $o\,o$, and the inner in the globe stem $i\,i$, separating the vapour and water in the steam-bath from that in the

globe, form the *saturation-gauge* to which reference has been made. So long as the steam in the globe A remains in a state of saturation, the inner column remains stationary, at a point a little above the level of the outer column, so as to balance the column of water in the steam-bath. But when, in raising the temperature, the whole of the water in A is evaporated, the steam becomes superheated, and then the pressure in A no longer balances the pressure in the steam-bath B, and the inner column of mercury rises and the outer one falls, the difference of level forming a measure of the expansion of the steam. It was found a matter of the greatest importance that the observer should not in these experiments trust to the unaided eye to determine the point at which the columns began to diverge, but that a careful series of measurements of the difference of level should be made, not only near the saturation point, but also at various temperatures of superheating; thus affording data for determining the law of expansion near the saturation point, and for estimating the maximum temperature of saturation from a point at which any error arising from the cohesion between the water and the glass, or from the retention of portions of water in the steam itself, might be eliminated. For reasons hereafter assigned, it was also found advisable to take these readings of the levels of the columns rather in a descending than in an ascending series of temperatures.

To read the column levels with rapidity and facility, seeing that they could not be approached within six or eight inches, a simple form of cathetometer was devised, sufficiently accurate for the purpose, and much more convenient than the complicated French instrument sometimes employed for this purpose. This cathetometer is shown in elevation, in Plate VIII. fig. 2; a is a heavy iron base resting on three levelling screws; into this is screwed firmly the planed iron stem $c\,c$, and adjusted by the levelling screws in a vertical position; on the stem slides a brass block, b, carrying a small telescope, $t\,t$, with sight wires, and fixed by a thumb-screw behind. Fig. 3 shows a part of the stem, $c\,c$, with the graduation into inches and tenths, the block b and vernier v moving with the telescope, by which the levels of the columns were read off to hundredths of an inch. In Plate VII. fig. 1, $f\,f$ shows the position of the cathetometer in the experiments, on its iron base or pedestal, g.

The steps in the process for determining the specific gravity of steam by this apparatus were as follows:—

A glass globule, of a size to contain as nearly as might be the required quantity of water for vaporization, was selected from a series similar in form to those shown in fig. 6, Plate VIII. In order to avoid the collision produced by the bursting of a sealed globule of water, as in Gay-Lussac's method, these globules had open stems, and after being filled with water were immersed hot in a cup of mercury (fig. 7), so that in cooling the mercury should rise and fill in part the capillary stem. The weight (w_1) of the cup, mercury and globule, all perfectly dry, was first ascertained by means of a delicate balance; the globule being then filled with water, the stem plunged in the mercury, and the surface of the mercury being dried, the weight (w_2) of the whole was determined. In this state the cup of mercury was transferred, and the globule passed into the large

globe, in which a Torricellian vacuum had been formed. Here the weight of water introduced $= w = w_2 - w_1$.

To form the Torricellian vacuum, the globe, filled with warm dry mercury, was heated upon a sand-bath until the mercury boiled; the stem was then filled with dry mercury and the globe inverted, with its stem inserted in a basin of mercury. The globule was then introduced into the stem, and allowed to ascend through the mercury column into the globe. In order to transfer the globe from the basin to its place in the steam-bath, a cap, *k* (Plate VIII. figs. 4 & 5), filled with mercury, was suspended from the stem by an india-rubber strap, a platinum wire being placed between the cap and globe-stem to ensure free passage for the mercury. The cover of the boiler, B B (Plate VII.), being then taken off, and the outer tube, *o o*, partially filled with dry mercury, the globe was raised and inserted into its place, resting on a tripod in the boiler, as shown in the diagram. The cover was then fixed with a flax and red-lead joint, and the cock *p* connected with a single barrel air-pump; exhaustion was effected so that the columns in the globe-stem and outer tube came nearly to a level; the air-pump was removed, and a portion of water allowed to enter through the cock. The gas-lights were then kindled, and until the water reached the boiling-point, the columns were maintained in position by the air-pump. The object of this, it will be seen, was to prevent any water passing round from the boiler to the globe. After boiling for a time the cock *p* was closed, and the process of vaporization went on simultaneously in the bath and globe, the temperature being kept sufficiently high in the oil-bath C C to maintain the water in the outer tube in a state of ebullition.

When all the parts of the globe have attained the same temperature as the steam in the bath, the mercury in the stem of the globe will stand a little above the mercury in the outer tube C C, the difference, *a b*, balancing the column of water, *b c*, and possibly the pressure of any air left in the steam-bath. The temperature of the baths is slowly and uniformly increased until the temperature of the vapour in the globe is considerably above the maximum temperature of saturation: after having been maintained for a considerable period at this temperature, the levels of the columns were observed; then, the temperature being allowed to sink some degrees, the operation was repeated, and the temperature again reduced until the columns became stationary, indicating saturated steam in the globe as well as the bath. The readings of a series of file marks on the globe-stem were taken at the same time, by which the capacity of the globe in each position of the mercury column could be calculated. All the elements were thus ascertained for calculating the density of the steam.

Let w be put for the weight of distilled water, at a temperature of 39°·1 Fahr., filling the globe to the point at which the mercury columns stood at the maximum temperature of saturation; let *w* be the weight of water vaporized; v = the specific volume of the steam, or the number of times the volume of steam exceeds the volume of the water from which it is raised; then

$$v = \frac{W}{w}. \qquad (3.)$$

By at once superheating the steam in the globe and then slowly reducing the temperature until the maximum temperature of saturation is reached, we secure the following advantages:—The cohesion of the water to the surface of glass being once overcome, that force of cohesion, it may be presumed, cannot be regained until the glass again becomes wet, which can only occur on condensation, that is, by the reduction of the temperature below that which corresponds to the maximum temperature of saturation. Moreover the observation of the columns at different temperatures of superheating, not only supplies us with data for determining the law of expansion of the superheated steam, but also data of verification or correction, as the case may be, of the point of maximum saturation determined by direct observation.

The results of the experiments show, *first*, that the density of saturated steam at all temperatures, above as well as below 212°, is invariably greater than that which is derived from the gaseous laws; *second*, that the law of expansion of a perfectly elastic fluid does not hold strictly true for superheated steam. At the maximum temperature of saturation, and for some degrees above it, the rate of expansion of the steam greatly exceeds that of a perfect gas.

Section I.—*Experiments at Pressures varying from fifteen to seventy pounds per square inch.*

In these experiments the thermometers were, it will be seen, exposed naked in the steam of the copper boiler, and this method offered the great advantage of rapidity in the indications of change of temperature round the globe, and enabled the observers, by constant and vigilant attention to the regulation of the supply of gas, to keep the temperature in the copper bath as nearly as possible uniform. But the thermometers, from exposure to pressure, require a correction. For this purpose the following experiments were obtained with simple water pressure.

Experiment 1.—*Thermometer* A.

Pounds pressure per square inch.	Temperature indicated.	Rise from pressure.
0	48°·2	——
20	48·8	0·6
40	49·1	0·9
60	49·5	1·3

Here the mean rise is 0°·022 for each pound of pressure above the atmosphere.

Experiment 2.—*Thermometer* B.

Pounds pressure per square inch.	Temperature indicated.	Rise from pressure.
0	198°·0	——
50	198·9	0·9

Here the rise is 0°·018 per pound pressure per square inch.

In the Tables of the experiments the temperatures are given as registered. In the summaries they are given reduced for pressure in the proportions above stated. No correction has been made to reduce the temperatures from the mercurial to the air-thermometer.

Capacity of Globes.

First. Globe A.—Water introduced =18009 grains at 63° FAHR. This corrected to 39°·1=18033 grains. Hence the capacity at the several file marks,—

Graduation:	First file mark	=18033 grains.
	Second file mark	=18159·2 grains.
	Third file mark	=18285·4 grains.
	Fourth file mark	=18411·6 grains.
	Fifth file mark	=18537·8 grains.

Second. Globe B.—Water introduced =17642 grains at 62°·5. Corrected to 39°·1=17663 grains.

Graduation:	First file mark	=17663 grains.
	Second file mark	=18420·4 grains.
	Third file mark	=18672·9 grains.
	Fourth file mark	=18925·3 grains.
	Fifth file mark	=19177·7 grains.

Third. Globe C.—Capacity taken with mercury equivalent to 18025 grains of water at 62° FAHR. Corrected to 39°·1=18046 grains.

Graduation:	First file mark	=18046 grains.
	Second file mark	=18298·4 grains.
	Third file mark	=18550·8 grains.
	Fourth file mark	=18803·2 grains.
	Fifth file mark	=18929·4 grains.
	Sixth file mark	=19055·6 grains.
	Seventh file mark	=19181·8 grains.

The following Tables give the results of the experiments between the ordinary atmospheric pressure and 60 lbs. per square inch. The first Table gives the observed results in full in each case, and the second gives a summary in which the column levels at the same temperature are averaged and corrections made for pressure in the thermometer bulb, expansion of mercury, &c.

Time.—The time between each reading is given as an indication of the reliability of the determinations of the column levels; changes of temperature could be made with great rapidity in the steam-bath, even without blowing off any steam, by lowering the gas-lights; but it required ten to fifteen minutes before the temperature of the glass globe had become uniform with the surrounding steam, and the columns had become stationary under the new temperature. When this was found to have taken place, a

series of readings was taken at intervals of three to five minutes, to obtain a reliable average, and the temperature again reduced.

Thermometers.—It was found necessary to maintain the temperature of the oil-bath considerably higher than that in the steam-bath, in order to make up for the radiation from the exposed portion of the tube and for the great retardation to the passage of the heat offered by the thick outer glass tube. The rule followed was to sustain such a temperature as would cause a gentle ebullition in the glass tube, trusting to the rapid convection of the water to secure a uniform temperature. No appreciable error could arise from this source from the smallness of the volume of steam in the globe-stem, and it was found in practice that a deposition of moisture almost immediately followed any cessation of the ebullition in the outer tube.

For another reason the necessity of a higher temperature in the oil-bath became a source of serious difficulty. The difference between the temperature of the water and oil required to be constantly increased as the temperature and pressure became higher, because the radiation increased in a higher ratio than could be prevented by the use of flannel coats, and a point was at last reached at which the unequal expansion of the thick glass tube on its cooler and warmer side, combined with the great pressure in its interior, caused a rupture attended by a dangerous explosion of great violence. Twice with glass tubes, which should have borne a pressure of 500 lbs., and each time under a pressure of only about 70 lbs. per square inch, an explosion occurred. In each case the fracture began in the bottom or closed end of the tube (unfortunately thickened by the glass-blower), as was evidenced by the boiler being lifted vertically from its seating, although the entire disruption of the tube immediately followed in the course of the explosion.

Temperature reduced for pressure.—This column is calculated from the observed temperatures according to the ratio arrived at in the experiments with water pressure. The thermometers were made expressly for these experiments at the Kew Observatory, and the graduation was accurate within the limits of errors of observation.

Capacity, in grains of water.—This column has been calculated from the readings on the cathetometer of the graduation marks, taken during each experiment. The capacity of the globe it is evident decreased as the inner column rose.

Difference of level has been corrected to 32° FAHR., at which temperature one atmosphere of pressure is assumed to be equivalent to 29·9218 inches of mercury.

Pressure of saturated steam, calculated from the experiments of M. REGNAULT.—This is evidently the pressure of the steam in the steam-bath; and if we deduct from this the column of mercury in the globe-stem which this pressure balances, we arrive at the pressure of the superheated steam in the glass globe, given in the next column.

Specific volume of the steam, obtained by dividing the capacity of the globe at each temperature by the quantity of water introduced.

In these experiments we were ably assisted by Mr. W. C. UNWIN; and we have much pleasure in stating that to his untiring zeal and superior skill in manipulation we are indebted for many important results.

Experiment 1.—Globe C. Thermometer A. March 8, 1859.
Weight of water introduced = 20·126 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m			inches.	inches.	inches.	
2 25	253°	264°	29·44	19·66	9·78	
2 30	253	.....	29·45	19·69	9·76	
2 40	253	.....	29·45	19·62	9·83	
2 45	253	.....	29·47	19·64	9·83	
2 50	253	.....	29·45	19·66	9·79	
2 55	253	.....	29·48	19·69	9·79	
3 18	251	262	28·13	20·24	7·89	
3 22	251	.....	28·10	20·26	7·84	
3 26	251	.....	28·00	20·18	7·82	
3 30	251	.....	28·16	20·15	8·01	
3 37	251	264	28·17	20·16	8·01	
3 42	251	.....	28·19	20·13	8·06	
4 0	249	260	26·72	20·63	6·09	
4 12	249	.....	26·58	20·68	5·90	
4 17	249	.....	26·59	20·63	5·96	
4 21	249	259	26·72	20·54	6·18	
4 25	249	.....	26·60	20·53	6·07	
4 30	249	.....	26·58	20·59	5·99	
4 55	246	258	24·62	21·24	3·38	
5 3	246	.....	24·70	21·16	3·54	Steam began to condense in globe-stem at $5^h\ 10^m$.
5 20	246	264	24·61	21·24	3·37	
5 23	246	.....	24·77	21·19	3·58	
5 26	246	.....	24·75	21·22	3·53	
5 32	244	280	23·71	21·57	2·14	
5 38	244	.....	23·62	21·60	2·02	
5 42	244	.....	23·46	21·60	1·86	
5 46	244	.....	23·58	21·52	2·06	
5 50	244	282	23·70	21·53	2·17	
6 10	243	282	23·36	21·67	1·69	
6 12	243	.....	23·30	21·69	1·61	
6 15	243	.....	23·30	21·68	1·62	
6 17	243	.....	23·38	21·64	1·74	
6 20	243	.....	23·31	21·65	1·66	
6 26	242	280	23·20	21·69	1·51	
6 30	242	.....	23·14	21·70	1·44	
6 35	242	.....	23·10	21·72	1·38	
6 40	242	.....	22·97	21·75	1·22	
6 45	242	.....	23·11	21·68	1·43	
6 50	242	268	23·16	21·68	1·48	
6 55	240	268	22·99	21·72	1·27	
7 0	240	.....	22·99	21·72	1·24	Condensation visible in globe-stem.

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
	inches.	inches.				inches.	inches.			
240°	22·99	1·26	2	239°·79	18938·2	1·24	.....	49·43	49·43	943·12
242	23·11	1·41	6	241·76	18929·8	1·38	0·14	52·53	52·39	942·72
243	23·33	1·67	5	242·75	18922·4	1·64	0·40	53·47	53·07	942·32
244	23·62	2·05	6	243·74	18908·9	2·01	0·77	54·43	53·66	941·67
246	24·69	3·48	5	245·72	18857·4	3·41	2·17	56·38	54·21	939·11
249	26·63	6·03	6	248·69	18771·4	5·90	4·66	59·42	54·76	934·86
251	28·12	7·93	6	250·67	18681·3	7·76	6·52	61·52	55·00	930·41
253	29·46	9·80	6	252·65	18609·8	9·59	8·35	63·68	55·33	926·91

Experiment 2.—Globe B. Thermometer A. March 3, 1859.

Weight of water introduced =21·193 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
4 20	254	290	29·42	20·52	8·90	
4 25	254	290	29·54	20·36	9·18	
4 30	254	290	29·54	20·32	9·22	
4 37	254	290	29·27	20·47	8·80	
4 45	254	290	29·56	20·34	9·22	
4 55	251	284	27·78	21·11		
5 3	251	284	27·53	21·14	6·39	
5 13	251	284	27·58	21·03	6·55	
5 15	251	284	27·50	21·16	6·34	
5 18	251	285	27·55	21·07	6·48	
5 25	251	285	27·32	21·19	6·13	
5 30	251	285	27·54	21·03	6·51	
6 0	248	273	25·41	21·80	3·61	
6 5	248	.....	25·40	21·81	3·59	
6 10	248	.....	25·61	21·66	3·95	
6 17	248	.....	25·26	21·87	3·39	
6 20	248	266	25·61	21·54	4·07	
6 35	245	278	23·94	22·13	1·81	
6 45	245	.....	24·02	22·08	1·97	
6 50	245	.....	23·98	22·06	1·92	
7 5	245	.....	24·04	22·04	2·00	No water visible in globe-stem.
7 17	245	.....	24·12	22·13	1·99	
7 22	245	262	23·98	22·02	1·96	
7 32	243	.....	23·73	22·14	1·59	
7 35	243	.....	23·69	22·12	1·57	
7 42	243	.....	23·74	22·12	1·62	No water visible in stem.
7 50	243	254	23·74	22·10	1·64	
7 57	241	.....	23·57	22·11	1·46	
8 5	241	.....	23·57	22·13	1·44	
8 20	244	.....	23·81	22·12	1·69	
8 25	244	.....	23·86	22·12	1·74	
8 30	245	260	24·10	22·06	2·04	
8 35	245	.....	24·11	22·06	2·05	
8 50	246	260	24·60	21·84	2·76	
9 0	246	.....	24·59	21·87	2·72	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for the expansion of glass.
°	inches.	inches.		°		inches.	inches.			
241	23·57	1·45	2	240·78	19200·3	1·42	.....	50·98	50·98	908·03
243	23·70	1·57	5	242·74	19198·8	1·54	0·12	53·47	53·35	907·98
244	23·83	1·71	2	243·72	19186·6	1·67	0·25	54·43	54·18	907·41
245	24·04	1·97	8	244·71	19177·0	1·93	0·51	55·40	54·89	906·94
246	24·59	2·74	2	245·70	19147·9	2·69	1·27	56·38	55·11	905·59
248	25·62	3·89	5	247·70	19097·8	3·81	2·39	58·41	56·02	903·25
251	27·54	6·44	7	250·67	18998·9	6·31	4·99	61·52	56·53	898·61
254	29·46	9·06	5	253·63	18893·2	8·87	7·45	64·69	57·24	893·64

Experiment 3.—Globe C. Thermometer A. December 8, 1858.

Weight of water introduced = 21·175.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
12 0	.....	.....	.....	.....	.....	Lamps lighted.
1 5	212	.....	30·33	20·30	10·03	Steam blowing off.
1 40	211·6	226	24·75	22·72	2·03	Steam-cock shut.
3 50	252	256	29·52	21·10	8·42	The differences in the cathetometer readings arise from the oscillation of the columns, which had to be read consecutively and not contemporaneously; partly perhaps from the obscuring of the real level in the outer tube by steam bubbles. These differences, however, are not great.
3 55	252	256	29·50	21·16	8·34	
4 0	252	255	29·65	21·14	8·51	
4 7	253	256	30·13	20·93	9·20	
4 18	253	265	30·16	21·00	9·16	
4 22	253	265	30·15	21·00	9·15	
4 37	251	262	28·94	21·36	7·58	
4 42	251	262	28·92	21·42	7·50	
4 50	250	260	28·50	21·68	6·82	
5 0	250	263	28·53	21·68	6·85	
5 10	249	262	27·98	21·73	6·25	
5 30	248	255	27·57	21·85	5·72	
5 50	247	268	27·09	21·99	5·10	
6 10	246	275	26·68	22·14	4·54	
6 25	245	272	26·43	22·25	4·18	
6 35	244	260	26·05	22·35	3·70	
6 40	244	257	26·22	22·32	3·90	
6 50	244	260	26·18	22·32	3·86	
7 40	244	265	26·20	22·31	3·89	
7 55	242	268	25·58	22·48	3·10	
8 0	242	268	25·56	22·50	3·06	
8 10	240	271	25·16	22·62	2·54	
8 20	242	271	25·56	22·52	3·04	
8 35	244	273	26·13	22·32	3·81	
8 45	246	274	27·01	22·15	4·86	
9 10	250	274	28·54	21·54	7·00	
9 30	252	277	29·79	21·12	8·67	
10 0	246	276	26·66	22·15	4·51	
10 8	245	274	26·42	22·22	4·20	
10 11	245	274	26·45	22·22	4·23	
10 20	247	.....	27·10	21·99	5·11	
10 23	247	.....	27·13	22·02	5·11	
10 30	244	276	26·14	22·34	3·80	
10 34	244	.....	26·18	22·33	3·85	
10 50	243	.....	25·94	22·45	3·49	
11 0	243	.....	25·90	22·35	3·55	
11 10	240	.....	25·28	22·56	2·72	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 30°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
°	inches.	inches.				inches.	inches.			
240	25·22	2·63	2	239·79	18856·6	2·58	.....	49·43	49·43	892·54
242	25·56	3·07	3	241·77	18840·5	3·01	0·43	52·53	52·10	891·74
243	25·92	3·34	2	242·76	18823·5	3·29	0·70	53·47	52·77	890·92
244	26·16	3·83	7	243·75	18812·1	3·76	1·18	54·43	53·25	890·40
245	26·43	4·19	2	244·74	18798·9	4·11	1·53	55·40	53·87	889·86
246	26·78	4·64	3	245·73	18780·1	4·55	1·97	56·38	54·41	888·98
247	27·11	5·11	3	246·72	18762·4	5·01	2·43	57·36	54·93	888·14
250	28·52	6·89	3	247·69	18686·7	6·75	4·17	60·52	56·35	884·60
252	29·61	8·48	4	251·66	18628·1	8·30	5·72	62·65	56·91	881·83
253	30·15	9·17	3	252·65	18599·1	8·98	6·40	63·68	57·28	880·46

Experiment 4.—Globe B. Thermometer A. March 11, 1859.

Weight of water introduced = 25·35 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
2 5	264	294	29·43	19·86	9·57	A more abundant command of heat was obtained in this than in preceding experiments.
2 10	264	.....	29·34	19·90	9·44	
2 15	264	.....	29·41	19·83	9·58	
2 20	264	.....	29·33	19·86	9·47	
2 25	264	285	29·37	19·81	9·56	
2 40	264	.....	29·30	19·86	9·44	
2 45	264	291	29·34	19·86	9·48	
2 51	261	294	27·30	20·65		
3 2	261	.....	26·90	20·71	6·19	
3 5	261	.....	27·02	20·66	6·36	
3 8	261	.....	26·98	20·70	6·28	
3 14	261	.....	26·95	20·71	6·24	
3 17	261	.....	26·89	20·71	6·18	
3 22	261	.....	26·94	20·71	6·23	
3 27	261	.....	26·90	20·71	6·19	
3 35	261	286	26·91	20·71	6·20	
4 0	259	.....	25·57	21·18	4·39	Interrupted for a short time.
4 35	259	.....	25·67	21·10	4·57	
4 43	259	290	25·50	21·12	4·38	
4 55	259	.....	25·54	21·18	4·36	
4 58	259	.....	25·54	21·14	4·40	
5 3	259	.....	25·52	21·11	4·41	
5 16	257	290	24·16	21·54	2·62	
5 20	257	.....	24·16	21·55	2·61	
5 25	257	.....	24·25	21·51	2·74	
5 30	257	.....	24·16	21·54	2·62	
5 35	257	.....	24·16	21·53	2·63	
5 40	257	300	24·16	21·51	2·63	
5 50	255	.....	23·35	21·76	1·59	
6 0	255	.....	23·32	21·71	1·61	
6 5	255	.....	23·35	21·71	1·64	
6 10	255	.....	23·36	21·70	1·66	
6 20	253	.....	23·14	21·79	1·35	
6 23	253	.....	23·14	21·79	1·35	
6 27	253	.....	23·14	21·80	1·34	
6 30	253	.....	23·17	21·79	1·38	
6 35	251	.....	23·16	21·78	1·38	
6 40	251	.....	23·12	21·77	1·35	
6 45	251	.....	23·14	21·79	1·35	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 30°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
°	inches.	inches.				inches.	inches.			
251	23·14	1·36	3	250·66	19206·4	1·34	.....	61·52	61·52	759·44
253	23·15	1·36	4	252·64	19206·4	1·34	.....	63·86	63·86	759·44
255	23·34	1·62	4	254·62	19196·4	1·60	0·26	65·89	65·63	759·06
257	24·17	2·64	6	256·60	19154·1	2·59	1·25	68·17	66·92	757·45
259	25·56	4·42	6	258·58	19082·5	4·32	2·98	70·52	67·54	754·62
261	26·93	6·23	8	260·54	19012·3	6·10	4·76	72·90	68·14	751·87
264	29·37	9·52	7	263·51	18878·0	9·30	7·96	76·64	68·68	746·70

Experiment 5.—Globe C. Thermometer A. December 10, 1858.

Weight of water in globe 29·145 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
1 0	.....	.....	.....	.....	.....	Lamps lighted.
5 25	273·2	300	32·22	20·18	12·04	
6 8	268	290	28·87	21·32	7·55	
6 14	268	289	28·55	21·41	7·14	
6 20	268	288	28·86	21·34	7·52	
6 43	264	286	26·60	22·10	4·50	
6 55	262	284	26·04	22·29	3·75	
7 0	262	284	26·11	22·27	3·84	
7 8	260	283				
7 15	260	285	25·48	22·44	3·04	
7 25	260	288	25·55	22·42	3·13	
7 42	256	293	24·77	22·68	2·09	
7 55	256	293	24·51	22·62	1·89	
9 0	273·2	315	32·31	20·08	12 23	
9 7	270	315	29·73	20·99	8·74	
9 12	268	315	28·41	21·39	7·02	
9 16	266	315	27·56	21·72	5·84	
9 22	264	310	26·51	22·06	4·45	
9 26	262	308	25·82	22·27	3·55	
9 33	260	.....	25·40	22·40	3·00	
9 38	260	.....	25·67	22·32	3·55	
9 58	264	.....	26·80	21·95	4·85	
10 10	266	300	27·80	21·55	6·25	
10 15	266	.....	27·64	21·62	6·02	
10 30	268	297	28·86	21·22	7·64	
10 35	268	.....	28·86	21·29	7·57	
11 7	273·2	310	32·35	19·94	12·41	

Summary of Column Determinations.

Mercurial thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
256°	inches. 24·64	inches. 1·99	2	255°·61	18876·0	inches. 1·95	inches.	67·03	67·03	649·24
260	25·52	3·18	4	259·56	18834·4	3·12	1·17	71·71	70·54	647·82
262	25·99	3·71	3	261·53	18814·1	3·63	1·68	74·09	72·41	647·65
264	26·63	4·60	3	263·50	18781·9	4·50	2·55	76·64	74·09	646·08
268	28·73	7·40	6	267·45	18666·3	7·23	5·28	81·84	75·56	642·12
270	29·73	8·74	1	269·41	18612·6	8·54	6·59	84·53	77·94	640·28
273·2	32·29	12·23	3	272·56	18475·1	11·95	10·00	89·01	79·01	635·59

Experiment 6.—Globe C. Thermometer A. March 12, 1859.

Weight of water introduced = 29·95 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
2 25	279	310	31·60	17·45	14·15	Lamps lighted at 11h 30m.
2 30	279	.....	31·59	17·40	14·19	
2 32	279	.....	31·60	17·35	14·25	
2 35	279	.....	31·62	17·46	14·16	
2 37	279	.....	31·64	17·36	14·28	
2 50	275	294	28·34	18·75	9·59	
3 5	275	.....	28·29	18·71	9·58	
3 8	275	.....	28·33	18·70	9·63	
3 15	275	.....	28·36	18·68	9·68	
3 16	275	.....	28·34	18·73	9·61	
3 19	275	.....	28·35	18·68	9·67	
3 22	275	.....	28·40	18·69	9·71	
3 30	271	290	24·71	19·96	4·75	
3 35	271	.....	24·67	19·95	4·72	
3 45	271	.....	24·78	19·78	5·00	No moisture could be detected in stem.
3 50	271	.....	24·78	19·78	5·00	
3 55	271	.....	24·91	19·78	5·13	
4 4	271	.....	24·74	19·83	4·91	
4 15	267	.....	22·38	20·52	1·86	
4 18	267	.....	22·30	20·57	1·73	
4 21	267	.....	22·38	20·52	1·86	
4 24	267	.....	22·37	20·50	1·87	
4 25	266	.....	22·28	20·53	1·75	
4 26	266	.....	22·26	20·56	1·70	
4 27	266	.....	22·26	20·53	1·73	
4 29	266	.....	22·26	20·51	1·75	
4 35	265	.....	22·11	20·58	1·53	
4 36	265	.....	22·18	20·55	1·63	
4 37	265	.....	22·16	20·54	1·62	
4 39	263	.....	22·02	20·58	1·44	Condensation became apparent in the stem at this temperature.
4 40	263	.....	.....	.....	.....	
4 43	263	.....	22·10	20·60	1·50	
4 45	263	.....	22·03	20·57	1·46	
4 47	263	.....	22·01	20·57	1·44	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
°	inches.	inches.		°		inches.	inches.			
263	22·04	1·46	4	262·52	18979	1·43	.....	75·37	75·37	635·30
265	22·16	1·60	3	264·49	18974	1·56	0·13	77·94	77·81	635·13
266	22·26	1·73	4	265·47	18970	1·69	0·26	79·24	78·98	635·00
267	22·36	1·83	4	266·46	18966	1·79	0·36	80·54	80·18	634·87
268	22·77	2·37	2	267·45	18948	2·32	0·89	81·84	80·95	634·28
271	24·76	4·95	6	270·40	18853	4·83	3·40	85·92	82·52	631·15
275	28·34	9·64	7	274·34	18657	9·41	7·98	91·62	83·64	624·62
279	31·61	14·19	5	278·27	18489	13·84	12·41	97·61	85·20	619·03

Experiment 7.—Globe B. Thermometer A. March 15, 1859.

Weight of water introduced = 31·730 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m			inches.	inches.	inches.	
2 20	279°	320°	31·64	20·16	11·48	Lamps lighted at 12 o'clock.
2 30	279	.....	31·63	20·14	11·49	
2 33	279	.....	31·74	20·16	11·58	
2 35	279	.....	31·70	20·14	11·56	
2 37	279	.....	31·58	20·14	11·44	
2 50	275	300	28·18	21·40	6·78	
2 54	275	.....	28·38	21·33	7·05	
2 57	275	.....	28·20	21·43	6·77	
3 0	275	.....	28·30	21·38	6·92	
3 7	275	300	28·26	21·38	6·88	
3 15	275	.....	28·36	21·41	6·95	
3 25	273	.....	26·38	22·02	4·36	
3 30	273	.....	26·30	22·02	4·28	
3 35	273	.....	26·45	22·00	4·45	
3 38	273	.....	26·36	22·01	4·35	
3 40	273	.....	26·40	22·01	4·39	
3 41	273	.....	26·38	22·02	4·36	
3 42	273	.....	26·41	22·02	4·39	
3 50	271	301	24·89	22·47	2·42	
3 56	271	.....	25·04	22·48	2·56	
4 0	271	.....	24·99	22·45	2·54	
4 3	271	.....	25·09	22·44	2·65	
4 4	271	.....	25·06	22·46	2·60	
4 6	271	.....	24·95	22·50	2·45	
4 10	271	.....	25·08	22·46	2·62	
4 55	267	310	23·93	22·79	1·14	
4 56	267	.....	23·95	22·79	1·16	
4 57	267	.....	23·98	22·77	1·21	
4 58	267	.....	23·95	22·79	1·16	
5 0	265	.....	23·81	22·80	1·01	
5 3	265	.....	23·89	22·78	1·11	
5 5	265	.....	23·95	22·78	1·17	
5 7	265	.....	23·89	22·75	1·14	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
	inches.	inches.				inches.	inches.			
265°	23·89	1·11	4	264°·49	19168·5	1·09	.....	77·94	77·94	605·65
267	23·95	1·19	4	266·46	19165·5	1·16	0·07	80·54	80·47	605·55
271	25·01	2·55	7	270·40	19111·2	2·50	1·41	85·92	84·51	603·90
273	26·38	4·37	7	272·36	19041·1	4·26	3·17	88·71	85·54	601·71
275	28·26	6·93	7	274·34	18934·5	6·76	5·67	91·62	85·95	598·34
279	31·65	11·51	5	278·27	18731·2	11·23	10·14	97·605	87·465	591·95

Experiment 8.—Globe A. Thermometer B. October 11, 1859.

Weight of water introduced = 31·58 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m			inches.	inches.	inches.	
4 30	282°	301°	22·72	12·32	10·40	Premature.
4 33	282	301	22·74	12·30	10·44	Premature.
4 37	282	301	22·68	12·30	10·38	Globe-stem dry.
4 43	282	300	22·66	12·35	10·31	
4 53	278	300	19·00	13·70	5·30	
5 0	278	297	19·01	13·67	5·34	
5 5	278	297	18·91	13·60	5·31	
5 10	278	297	18·90	13·63	5·27	
5 15	278	297	18·85	13·62	5·23	On sinking to 276°, moisture became visible in stem at 5h 25m, the temperature was therefore raised again.
5 55	278	307	19·00	13·70	5·30	
5 58	278	.....	18·85	13·70	5·15	
6 0	278	304	18·85	13·74	5·11	
6 8	276	.....	17·47	14·16	3·31	A trace of moisture perceptible.
6 15	276	.....	17·45	14·17	3·28	
6 17	276	308	17·40	14·21	3·19	
6 19	276	.....	17·50	14·17	3·33	
6 23	276	.....	17·40	14·11	3·29	Moisture still preserved.
6 33	274	.....	16·66	14·34	2·32	
6 35	274	.....	16·60	14·34	2·26	
6 40	274	.....	16·80	14·35	2·45	
6 45	274	.....	16·70	14·28	2·42	
6 50	274	.....	16·70	14·33	2·37	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity, of globe, in grains of water at 30°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
	inches.	inches.				inches.	inches.			
274°	16·69	2·36	5	273°·48	18406·7	2·31	.....	90·35	90·35	584·44
276	17·44	3·28	5	275·46	18372·9	3·20	0·89	93·29	92·40	583·37
278	18·92	5·25	8	277·43	18306·1	5·13	2·82	96·30	93·48	581·26
282	22·67	10·34	2	281·38	18118·1	10·09	7·78	102·56	94·78	574·00

Experiment 9.—Globe A. Thermometer B. October 14, 1859.

Weight of water introduced = 34·01 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m			inches.	inches.	inches.	
4 15	289°	318°	24·13	12·12	12·01	Lamps lighted at 2 o'clock. Water boiling at 3 o'clock.
4 17	289	.....	24·30	12·10	12·20	
4 20	289	.....	24·22	12·12	12·10	
4 25	289	.....	24·29	12·12	12·17	
4 27	289	.....	24·20	12·07	12·13	
4 30	289	316	24·26	12·06	12·20	
4 47	285	314	20·70	13·63	7·07	
4 49	285	.....	20·75	13·64	7·11	
4 51	285	.....	20·65	13·63	7·02	
4 53	285	.....	20·65	13·60	7·05	
4 56	285	.....	20·66	13·60	7·06	
5 0	285	315	20·72	13·64	7·08	
5 5	283	.....	18·82	14·24	4·58	
5 10	283	.....	18·85	14·22	4·63	
5 14	283	.....	18·84	14·25	4·59	
5 17	283	.....	18·90	14·25	4·65	
5 19	283	.....	18·90	14·26	4·64	
5 21	283	.....	18·86	14·29	4·57	
5 30	278	.....	16·65	15·10	1·55	
5 33	278	.....	16·64	15·10	1·54	
5 35	278	.....	16·66	15·09	1·57	
5 40	274	.....	16·44	15·11	1·33	
5 42	274	.....	16·50	15·13	1·37	
5 45	274	.....	16·45	15·10	1·35	
5 50	274	.....	16·43	15·05	1·38	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity, of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam, corrected for expansion of glass.
	inches.	inches.				inches.	inches.			
289°	24·23	12·13	6	288°·25	18040·1	11·78	10·45	114·24	103·79	531·96
285	20·69	7·06	6	284·32	18235·4	6·86	5·53	107·44	101·91	537·68
283	18·86	4·61	6	282·34	18319·7	4·48	3·15	104·14	100·99	540·17
278	16·65	1·55	3	277·43	18415·4	1·51	0·18	96·30	96·12	542·91
274	16·45	1·36	4	273·48	18423·8	1·33	.....	90·35	90·35	543·17

Experiment 10.—Globe B. Thermometer A. December 14, 1858.

Weight of water introduced = 37·58 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
12 45	285	316	.....	19·50	.....	
2 15	285	304	30·20	22·63	7·57	
2 20	285	307	30·73	22·42	8·31	Probably erroneous.
2 30	285	330	30·20	22·64	7·56	
2 40	285	325	29·53	23·01	6·52	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.
	inches.	inches.				inches.	inches.
Max. desc.	24·33 ?	2·50 ?	.....	.....	18930	2·45 ?	.....
285°	29·98	7·21	4	284·16	18872	7·04	4·59

After obtaining these determinations, and whilst the experiment was incomplete, the oil-bath cracked at the bottom and stayed further progress. In consequence of having these vessels so deep, difficulty was found in getting them blown, and we had to be content with such as could be obtained. These were very thick at the bottom, where the heat was greatest and danger most to be apprehended, and in consequence at the higher pressures they became a fertile source of annoyance.

Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
.....	.....	514·98
107·17	102·58	503·60

Experiment 11.—Globe B. Thermometer A. March 19, 1859.

Weight of water introduced = 38·745 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m			inches.	inches.	inches.	
2 25	291°	320°	31·04	19·40	11·64	Lamps lighted at 11h 45m.
2 28	291	.....	31·02	19·42	11·60	
2 30	291	.....	30·97	19·44	11·53	
2 40	287	.....	26·85	20·78	6·07	
2 45	287	.....	27·00	20·85	6·15	
2 53	287	.....	26·72	20·78	5·94	
3 0	287	.....	26·74	20·77	5·97	
3 20	285	320	24·90	21·34	3·56	
3 25	285	.....	24·80	21·33	3·47	
3 30	285	.....	24·85	21·34	3·51	
3 35	285	.....	24·85	21·37	3·48	
3 50	284	.....	24·20	21·59	2·61	
3 55	284	.....	24·15	21·56	2·59	
4 0	284	.....	24·19	21·56	2·63	
4 4	284	.....	24·13	21·58	2·55	
4 10	284	.....	24·20	21·52	2·68	
4 17	283	.....	23·74	21·70	2·04	
4 30	283	.....	23·80	21·66	2·14	
4 34	283	.....	23·75	21·65	2·10	
4 40	283	.....	23·79	21·64	2·15	
4 50	282	.....	23·46	21·75	1·71	
4 57	282	.....	23·46	21·72	1·74	
5 3	282	.....	23·50	21·76	1·74	
5 8	281	316	23·10	21·79	1·31	
5 13	281	.....	23·37	21·71	1·66	
5 20	281	.....	23·41	21·74	1·67	
5 23	281	.....	23·38	21·76	1·62	
5 30	279	.....	23·29	21·79	1·50	
5 35	279	.....	23·16	21·79	1·37	
5 40	279	.....	23·30	21·82	1·48	
5 45	275	.....	23·00	21·83	1·17	
5 43	275	.....	23·05	21·87	1·18	
5 50	275	.....	23·00	21·85	1·15	
5 55	275	.....	23·00	21·86	1·14	
6 0	275	.....	22·93	21·91	1·02	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity, of globe, in grains of water at 39°·1	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
	inches.	inches.				inches.	inches.			
275°	23·00	1·14	5	274°·34	19214·0	1·11	.....	91·62	91·62	497·25
279	23·25	1·45	3	278·27	19201·2	1·42	0·31	97·61	97·30	496·91
281	23·31	1·56	4	280·24	19197·9	1·53	0·42	100·73	100·31	496·83
282	23·47	1·73	3	281·22	19189·9	1·69	0·58	102·31	101·73	496·63
283	23·77	2·11	4	282·20	19174·7	2·06	0·95	103·91	102·96	496·24
284	24·17	2·61	5	283·18	19154·2	2·55	1·44	105·53	104·09	495·71
285	24·88	3·51	4	284·16	19117·8	3·42	2·31	107·17	104·86	494·81
287	26·82	6·03	4	286·13	19018·4	5·98	4·87	110·53	105·66	491·12
291	31·01	11·59	3	290·05	18771·9	11·30	10·29	117·47	107·18	485·91

Experiment 12.—Globe B. Thermometer A. March 24, 1859.

Weight of water introduced = 41·877 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
3 36	295	325	30·94	20·84	10·10	Lamps lighted at 12 o'clock.
3 40	295	.....	31·02	20·81	10·21	
3 45	295	.....	31·03	20·77	10·26	
3 48	295	.....	30·91	20·84	10·07	
3 51	295	.....	30·91	20·89	10·02	
3 54	295	.....	30·96	20·87	10·09	
4 35	295	320	31·02	20·81	10·21	
4 0	291	320	27·00	22·22	4·78	
4 8	291	.....	27·03	22·23	4·80	
4 50	291	.....	26·95	22·20	4·75	
4 55	291	.....	27·03	22·22	4·81	
4 57	291	.....	27·00	22·17	4·83	
5 5	290	.....	26·40	22·43	3·97	
5 10	290	.....	26·42	22·44	3·98	
5 12	290	.....	26·40	22·39	4·01	
5 25	287	.....	25·00	22·84	2·16	
5 26	287	.....	25·04	22·87	2·17	
5 28	287	.....	24·89	22·90	1·99	
5 30	287	.....	25·00	22·83	2·17	
5 35	285	.....	24·55	22·89	1·66	
5 40	285	.....	24·62	22·93	1·69	
5 42	285	.....	24·66	22·98	1·68	
5 43	285	.....	24·67	23·01	1·66	
5 45	285	.....	24·58	23·02	1·56	
5 50	283	.....	24·39	23·07	1·32	
5 53	283	.....	24·43	23·10	1·33	
5 55	283	.....	24·50	23·06	1·44	
5 57	283	.....	24·51	23·06	1·45	
6 0	281	.....	24·36	23·09	1·27	
6 3	281	.....	24·38	23·11	1·27	
6 5	281	.....	24·33	23·11	1·22	
6 36	293	.....	29·56	21·40	8·16	
6 38	293	.....	29·62	21·43	8·19	
6 40	293	.....	29·51	21·40	8·11	
6 45	293	.....	29·52	21·41	8·11	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
°	inches.	inches.		°		inches.	inches.			
281	24·36	1·26	3	280·24	19150·0	1·23	.....	100·73	100·73	458·30
283	24·46	1·39	4	282·20	19144·9	1·36	0·13	103·91	103·78	458·44
285	24·61	1·65	5	284·16	19137·2	1·62	0·39	107·17	106·78	458·25
287	24·98	2·12	4	286·13	19118·1	2·08	0·85	110·53	109·68	457·79
290	26·40	3·98	3	289·07	19045·1	3·88	2·65	115·70	113·05	456·10
291	27·00	4·79	6	290·05	19014·2	4·67	3·44	117·47	114·03	455·34
293	29·55	8·14	4	292·02	18872·3	7·94	6·71	121·11	114·40	451·95
295	30·97	10·14	6	293·97	18780·3	9·88	8·65	124·75	116·10	449·72

Experiment 13.—Globe A. Thermometer B. October 19, 1859.

Weight of water introduced = 42 680 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m			inches.	inches.	inches.	
1 33	302°	339°	23·27	12·86	10·41	
1 35	302	.....	23·22	12·86	10·36	
1 37	302	.....	23·26	12·86	10·40	
1 42	302	336	23·25	12·83	10·42	
1 53	299	329	19·97	13·91	6·06	
1 57	299	.....	19·98	13·85	6·13	
2 0	299	.....	19·93	13·84	6·09	
2 5	299	330	19·96	13·85	6·11	
2 8	299	.....	19·89	13·83	6·06	
2 10	299	.....	19·94	13·85	6·09	
2 20	297	.....	17·94	14·27	3·67	
2 25	297	.....	18·00	14·27	3·73	
2 27	297	327	17·90	14·25	3·65	
2 30	297	.....	18·03	14·23	3·80	
2 35	297	.....	17·95	14·24	3·71	
2 43	293	.....	16·44	14·72	1·72	
2 47	293	.....	16·44	14·69	1·75	
2 49	293	.....	16·43	14·73	1·70	
2 51	293	.....	16·47	14·72	1·75	
2 58	289	.....	16·39	14·80	1·59	
3 0	289	.....	16·36	14·82	1·54	
3 5	289	.....	16·40	14·82	1·58	
3 10	289	.....	16·39	14·76	1·63	

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Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.	Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
289°	inches. 16·39	inches. 1·59	4	288°·25	18433·8	inches. 1·55	inches.	114·24	114·24	433·12
293	16·44	1·73	4	292·19	18431·8	1·68	0·13	121·40	121·27	433·08
297	17·96	3·71	5	296·13	18364·7	3·60	2·05	128·92	126·87	431·50
299	19·94	6·09	6	298·09	18268·3	5·91	4·36	132·80	128·44	429·28
302	23·25	10·40	4	301·03	18097·1	10·09	8·54	138·78	130·24	425·41

Experiment 14.—Globe A. Thermometer A. April 6, 1859.

Weight of water introduced =41·069 grains.

Time.	Thermometer.		Cathetometer.		Difference of level of columns.	Remarks.
	In steam.	In oil.	Inner column.	Outer column.		
h m	°	°	inches.	inches.	inches.	
2 10	297	348	31·88	19·40	12·48	Premature.
2 15	297	.....	31·78	19·38	12·40	Premature.
2 18	297	.....	31·50	19·40	12·10	
2 20	297	.....	31·64	19·38	12·26	
2 22	297	.....	31·60	19·38	12·22	
2 24	297	.....	31·79	19·30	12·49	
2 28	297	.....	31·50	19·35	12·15	
2 30	297	.....	31·38	19·50	11·88	
2 45	297	.....	31·25	19·59	11·66	

Summary of Column Determinations.

Thermometer, Fahr.	Cathetometer, inner column.	Difference of level of columns.	Number of determinations averaged.	Temperature, corrected for pressure.	Capacity of globe, in grains of water at 39°·1.	Difference of level of columns, corrected to 32°.	Rise of column from point of maximum descent.
°	inches.	inches.	.....	°	18414	inches. 1·5	inches. .....
297	31·52	12·11	7	295·93	18011·2	11·79	10·29

This experiment was arrested whilst incomplete by the breaking of the thermometer.

Pressure of saturated steam, in inches of mercury.	Pressure of steam in globe, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
.....	.....	449·62
128·40	118·11	439·85

Reduction of the preceding Experiments.

The inner column of mercury having attained its maximum point of descent, remains stationary so long as vaporization is going on in both vessels, and then the temperature at which the first decided indication of ascent of the inner column is observed, obviously gives us the maximum temperature of saturation. Thus, for example, in Experiment 2, we should at once fix this temperature at, or nearly at, 244°·71; for at this temperature the inner column of mercury stands about half an inch above the level corresponding to saturation pressure, the differences of level at less temperatures being too small to warrant us in taking them as indications of superheating. But as slight oscillations in this column, arising from accidental changes of temperature or from other causes, might lead us to infer that the steam had arrived at its maximum temperature of saturation before it had actually attained this point, we considered that there would be less chance of

error, if this point were in all cases determined by a reduction taken from observations made at a point of temperature somewhat above that of saturation.

For small ranges of temperature, we may presume that the relation expressed by equation (1) will apply within small limits of error to superheated steam. Let V_1, p_1, t_1 be the specific volume, pressure, and temperature, respectively, of a given weight of steam when superheated; then we find

$$V_1 p_1 - V_2 p_2 = \alpha(t_1 - t_2), \quad \ldots \quad (4.)$$

where the constant $\alpha = 74{\cdot}8$ nearly. Moreover, let T_1 be the maximum temperature of saturation of the steam, and V_1 its corresponding specific volume, then, from equation (1), we get

$$V_1 P_1 = V_2 p_2 + \alpha(T_1 - t_2), \quad \ldots \quad (5.)$$

and hence

$$P_1 = \frac{V_2 p_2}{V_1} + \frac{\alpha}{V_1}(T_1 - t_2). \quad \ldots \quad (6.)$$

Now having given from the Tables of the experiments the values of V_2, p_2, t_2, and taking V_1 as the specific volume at the maximum descent of the mercury, the value of T_1 may be assumed with a near approach to accuracy from the indications in the experiments; then, if the value of P_1 deduced from this assumption coincide with the pressure of saturated steam at that temperature, the maximum temperature of saturation has been rightly assumed. If not, the value of T_1 deduced from the value of P_1 given by the equation may be taken for a second approximation, and so on till the value of P_1 does coincide with the pressure of saturated steam deduced from the experiments of M. Regnault.

The following Table gives the temperature of saturation thus deduced from the preceding experimental Tables, the two highest temperatures of superheating being in most cases assumed as the data for calculation. In one or two cases, where the lower of these two temperatures is manifestly within the limits of imperfect expansion, the reduction from the higher temperature alone has been retained.

The point thus determined (strictly speaking) is the temperature of maximum saturation of the steam, assuming that at this point it retains all its watery vapour in an aëriform state. This ideal point of temperature, it must be observed, will always be a trifle higher than the actual point. As the coefficient α is always small as compared with V_1, the value of P_1, in equation (6.), is not much affected by any possible variations of value which may be given to this coefficient.

TABLE of Results, deduced from the preceding determinations of the maximum temperature of saturation and specific volume of steam, at pressures of from 15 to 70 lbs. per square inch.

Number of Exper.	Maximum temperature of saturation, Fahrenheit.		Pressure of steam, in inches of mercury.		Specific volume of the steam.	Maximum temperature of saturation, Centigrade.	Pressure of steam, in millimetres of mercury.
	°	°				°	
1.	242·89	242·90	53·60	53·61	943·12	117·16	1361·7
	242·92		53·63				
2.	244·90	244·82	55·60	55·52	908·03	118·23	1410·1
	244·74		55·44				
3.	245·42	245·22	56·08	55·89	892·54	118·45	1419·6
	245·02		55·70				
4.	255·37	255·50	66·70	66·84	759·44	124·16	1697·7
	255·62		66·97				
5.	263·20	263·14	76·26	76·20	649·24	128·41	1935·4
	263·09		76·13				
6.	267·35	267·21	81·71	81·53	635·30	130·67	2070·8
	267·08		81·36				
7.	269·24	269·20	84·36	84·20	605·65	131·77	2138·9
	269·16		84·25				
8.	274·76		92·23		584·44	134·86	2342·6
9.	273·30		90·08		543·17	134·05	2287·9
10.	279·42		99·60		514·98	137·45	2529·8
11.	282·55	282·58	104·48	104·54	497·25	139·21	2655·2
	282·61		104·60				
12.	287·49	287·25	112·82	112·78	458·30	141·80	2864·6
	287·00		112·75				3105·1
13.	292·53		122·25		433·12	144·74	
14.	288·25		114·25		449·62	142·36	2901·9

SECTION II.—*Experiments at Pressures less than that of the Atmosphere.*

As there would be a difficulty in maintaining the copper steam-bath perfectly air-tight when the elasticity of the steam is considerably less than that of the atmosphere, the construction of the apparatus was modified in the following manner:—

The extremity of the stem of the glass globe, passing through the outer tube, had its extremity inserted in a deep mercury-bath, the surface of which was exposed to the pressure of the atmosphere. The elevation of the column of mercury in the globe-stem above the level of the mercury in the bath being taken at different temperatures, and the corresponding elevation of the mercury in the barometer being observed, the difference of these two columns at once gives the elasticity of the vapour in the globe for the corresponding temperature. The maximum temperature of saturation, in this case, takes place at that point where the column of mercury, measuring the elasticity of the vapour in the globe, begins to deviate from the column of pressure measuring the elasticity of saturated steam.

Plate VIII. fig. 1 is a section of the copper boiler and apparatus arranged for the low-pressure experiments. B is the copper boiler, with its cover removed and supported on the strong tripod as before ; *o o* the outer glass tube 1½ inch diameter and 32 inches long, fixed as before in the stuffing-box *s*, but in these experiments open at the bottom,

and after the insertion of the globe A, closed by an india-rubber cork. C C is the large mercury-bath for heating the glass tube, with its lamp *h*, and shade of sheet iron *k*: the globe A rests on a tripod, *n*, in the copper bath, and its stem passing down through the outer tube, is open at bottom in the mercury-bath. To transfer this globe from its place over the basin in which it has been inverted, to form the Torricellian vacuum to the boiler, the cap of india-rubber (fig. 9) is placed over the end. A small block of wood, *x*, fixed by a wedge, slides over the outer tube and carries a double-pointed screw, by which the level of the mercury in the bottom bath could be read off by the cathetometer, the length of the screw being added to the height taken from the upper point. A frame of wood carried the two thermometers *t* and *t'* placed above and below the globe in the copper bath. The boiler was heated by gas-jets, E, as before. The difficulty arising from the retardation of the passage of heat through the outer glass tube, already alluded to, was found in an increased degree in these experiments, owing to the small surface exposed to the heat of the mercury-bath. After the fracture of two or three tubes, which from their large size were very imperfectly annealed, an iron tube, *p*, was cemented to the lower part of the glass, and entirely removed the difficulty. It enabled a violent ebullition to be maintained in the glass tube, if necessary, at more than twenty degrees lower temperature in the mercury than before.

The globes were filled with mercury, inverted, and the water introduced as before.

Capacity of Globe G.

Water introduced =18425 grains at 50° FAHR., this reduced to 39°·1 =18427 grains.

Graduation:	First file mark . .	=18427·0 grains.
	Second file mark . .	=18553·2 grains.
	Third file mark . .	=18679·4 grains.
	Fourth file mark . .	=18805·6 grains.
	Fifth file mark . .	=18931·8 grains.

The utmost care was taken throughout the experiments to prevent the admission of air or any other influence likely to affect the accuracy of the results.

Experiment 1.—Globe G. Thermometers B and C. November 16, 1859.

Weight of water introduced = 2·215 grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr. °	Fahr. °	Fahr. °	inches.	inches.	inches.
4 35	170	170	227	29·28	4·37	24·91
4 40	170	170	222	29·28	4·37	24·91
4 43	170	170	222	29·28	4·37	24·91
4 45	170	170	226	29·28	4·37	24·91
5 20	140	140	227	29·54	4·37	25·17
5 25	140	140	228	29·53	4·37	25·16
5 28	140	140	228	29·56	4·37	25·19
5 30	140	140	228	29·56	4·37	25·19
5 50	136	136	224	29·64	4·34	25·30
5 53	136	136	224	29·71	4·34	25·37
5 55	136	136	225	29·67	4·34	25·33
6 5	133	133	226	30·04	4·34	25·70
6 10	133	133	226	30·06	4·34	25·72
6 15	132	132	228	30·23	4·34	25·89
6 17	132	132	230	30·22	4·34	25·88
6 19	132	132	230	30·22	4·34	25·88

The barometer reading during this experiment (corrected to 32°) was 30·15.

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1	Difference of level of columns, in inches.	Difference of level of columns, corrected to 32°, in inches.	Elastic force of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
132°	3	30·22	18289	25·88	25·42	4·72	4·72	8265·3
133	2	30·05	18297	25·71	25·27	4·87	4·85	8269·2
136	3	29·67	18310	25·33	24·90	5·24	5·25	8275·3
140	4	29·55	18313	25·18	24·75	5·39	5·83	8278·4
170	4	29·28	18322	24·91	24·48	5·66	12·16	8284·4

Experiment 2.—Globe G. Thermometers B and C. November 11, 1859.

Weight of water introduced = 3·455 grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr. °	Fahr. °	Fahr. °	inches.	inches.	inches.
11 25	190	190	265	26·42	4·77	21·65
11 30	190	190	263	26·42	4·77	21·65
11 35	190	190	267	26·42	4·77	21·65
11 37	190	190	266	26·42	4·77	21·65
11 40	190	190	266	26·41	4·77	21·64
11 55	180	180	270	26·59	4·77	21·82
12 0	180	180	268	26·59	4·77	21·82
12 5	180	180	268	26·59	4·77	21·82
12 20	170	170	276	26·76	4·80	21·96
12 25	170	170	274	26·75	4·80	21·95
12 27	170	170	274	26·76	4·80	21·96
12 30	170	170	270	26·76	4·80	21·96
12 47	160	160	284	26·92	4·80	22·12
12 57	160	160	284	26·92	4·80	22·12
1 15	150	150	280	28·05	4·80	23·25

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
150°	1	28·05	18364·4	23·25	22·91	7·53	7·52	5321·9
160	2	26·92	18402·5	22·12	21·79	8·65	9·61	5333·5
170	4	26·76	18407·9	21·96	21·63	8·81	12·16	5336·1
180	3	26·59	18413·5	21·82	21·49	8·95	15·26	5338·1
190	5	26·42	18420·7	21·65	21·33	9·11	18·99	5341·2

The barometer read from 30·44 to 30·45 during this experiment.

Experiment 3.—Globe G. Thermometers B and C. November 7, 1859.

Weight of water introduced = 3·76 grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr.°	Fahr.°	Fahr.°	inches.	inches.	inches.
1 5	209·9	.....	264	24·26	4·83	19·43
1 20	209·9	209·9	258	24·22	4·83	19·39
1 25	209·9	209·9	260	24·22	4·83	19·39
1 30	206	206·5	268	24·36	4·83	19·53
1 40	206	206·5	271	24·26	4·83	19·43
1 45	206	206·5	.....	24·27	4·83	19·44
1 48	206	206·5	272	24·26	4·83	19·43
1 50	206	206·5	272	24·26	4·83	19·43
2 10	198	198·4	265	24·39	4·82	19·57
2 15	198	198·5	265	24·38	4·82	19·56
2 20	198	198·4	266	24·38	4·83	19·55
2 25	198	198·4	270	24·38	4·82	19·56
2 41	190	190·5	270	24·50	4·82	19·68
2 45	190	190·5	266	24·51	4·82	19·69
2 49	190	190·5	270	24·47	4·82	19·65
3 2	180	180·4	268	24·67	4·82	19·85
3 8	180	180·4	268	24·67	4·82	19·85
3 11	180	180·4	268	24·67	4·82	19·85
3 25	170	170·4	273	24·84	4·82	20·02
3 30	170	170·4	268	24·82	4·82	20·00
3 33	170	170·4	269	24·82	4·82	20·00
3 50	160	160·1	270	25·03	4·82	20·21
3 55	160	160·1	270	25·00	4·82	20·18
4 0	160	160·1	260	25·00	4·82	20·18
4 17	155	155·1	280	25·93	4·82	21·11
4 25	155	155·1	285	25·95	4·82	21·13
4 27	155	155·1	280	25·93	4·82	21·11
4 30	155	155·1	280	25·90	4·82	21·08
4 35	155	155·1	280	25·94	4·82	21·12
4 41	155	155·1	280	25·95	4·82	21·13
4 52	157	157·2	280	25·53	4·82	20·71
4 55	157	157·2	280	25·52	4·82	20·70
5 0	157	157·2	280	25·53	4·82	20·71
5 7	159	159·3	280	25·18	4·82	20·36
5 10	159	159·4	280	25·19	4·82	20·37
5 15	159	159·4	275	25·18	4·82	20·36
5 25	160	160	276	25·07	4·82	20·25

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
155°·0	6	25·93	18447·2	21·11	20·86	8·52	8·51	4911·9
157·1	3	25·53	18460·7	20·71	20·46	8·93	8·96	4915·7
159·2	3	25·18	18472·4	20·36	20·12	9·28	9·42	4918·7
160·0	4	25·02	18477·9	20·20	19·97	9·32	9·61	4920·2
170·2	3	24·82	18484·5	20·00	19·76	9·61	12·21	4922·6
180·2	3	24·67	18489·6	19·85	19·60	9·77	15·31	4924·9
190·2	3	24·49	18495·8	19·67	19·42	9·94	19·06	4927·0
198·2	4	24·38	18499·3	19·56	19·31	10·04	22·59	4928·4
206·2	5	24·28	18502·7	19·45	19·20	10·14	26·67	4930·0
209·9	2	24·22	18504·7	19·39	19·14	10·21	28·69	4930·7

The barometer read from 29·34 to 29·40 during this experiment.

Experiment 4.—Globe G. Thermometers B and C. November 12, 1859.

Weight of water introduced = 4·985 grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr.°	Fahr.°	Fahr.°	inches.	inches.	inches.
1 0	211	211	280	21·54	4·45	17·09
1	211	211	285	21·54	4·45	17·09
1 25	190	190	285	21·96	4·45	17·51
1 30	190	190	285	21·96	4·45	17·51

At this point progress was stayed by the cracking of the outer tube.

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
170°	.....	.....	18529	17·90	17·98	12·16	12·16	3722·6
190	2	21·96	18516	17·51	17·26	12·88	18·99	3720·9
211	2	21·54	18508	17·09	16·84	13·30	29·41	3720·3

The barometer (corrected to 32° FAHR.) read during this experiment 30·14 inches.

Experiment 5—Globe G. Thermometers B and C. November 14, 1859.

Weight of water introduced =5·000 grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr.°	Fahr.°	Fahr.°	inches.	inches.	inches.
4 40	200	200	225	21·87	4·38	.....
4 45	200	200	226	21·82	4·38	.....
4 50	200	200	222	21·60	4·38	17·22
5 0	200	200	224	21·60	4·38	17·22
5 3	200	200	224	21·60	4·38	17·22
5 22	180	180	226	22·00	4·38	17·62
5 25	180	180	225	21·99	4·38	17·61
5 27	180	180	225	21·98	4·38	17·60
5 30	180	180	225	21·98	4·38	17·60
5 40	170	170	226	22·57	4·38	18·19
5 45	170	170	224	22·61	4·38	18·23
5 48	170	170	225	22·59	4·38	18·21
5 50	170	170	225	22·58	4·38	18·20
5 53	170	170	226	22·58	4·38	18·20
6 5	168	168	227	23·11	4·38	18·73
6 8	168	168	227	23·12	4·38	18·74
6 10	168	168	227	23·18	4·38	18·80
6 13	168	168	227	23·15	4·38	18·77
6 15	168	168	.....	23·18	4·38	18·80
6 18	168	168	.....	23·15	4·38	18·77

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
168°	6	23·15	18529·0	18·77	18·45	11·61	11·61	3711·3
170	5	22·60	18547·5	18·21	17·91	12·15	12·16	3715·1
180	4	21·99	18557·9	17·61	17·29	12·77	15·26	3717·6
200	3	21·69	18581·0	17·22	16·88	13·18	23·45	3723·3

The barometer (corrected to 32° FAHR.) read during this experiment 30·06 inches.

Experiment 6.—Globe G. Thermometers B and C. November 17, 1859.

Weight of water introduced $=2{\cdot}215+3{\cdot}20=5{\cdot}415$ grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr. °	Fahr. °	Fahr. °	inches.	inches.	inches.
11 18	200	200	222	20·50	4·35	16·15
11 21	200	200	226	20·51	4·35	16·16
11 25	200	200	226	20·50	4·35	16·15
11 27	200	200	226	20·50	4·35	16·15
11 30	200	200	226	20·49	4·35	16·14
11 45	180	180	228	20·89	4·35	16·54
11 48	180	180	226	20·90	4·35	16·55
11 50	180	180	226	20·91	4·35	16·56
11 53	180	180	226	20·91	4·35	16·56
11 55	180	180	228	20·90	4·35	16·55
12 10	174	174	228	21·31	4·35	16·96
12 13	174	174	228	21·31	4·35	16·96
12 16	174	174	227	21·35	4·35	17·00
12 19	174	174	226	21·33	4·35	16·98
12 24	174	174	229	21·41	4·35	17·06
12 30	174	174	230	21·35	4·35	17·00
12 44	169	169	226	22·71	4·33	18·38
12 48	169	169	225	22·70	4·33	18·37
12 52	169	169	225	22·72	4·33	18·39
12 55	169	169	225	22·76	4·33	18·43
12 58	169	169	225	22·70	4·33	18·37
1 0	169	169	228	22·76	4·33	18·43

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem.	Capacity of globe, in grains of water at 39°·1, in inches.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 39°·1, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
169°	6	22·72	18542·1	18·39	18·13	11·88	11·88	3429·4
174	6	21·34	18588·5	16·99	16·73	13·28	13·33	3438·1
180	5	20·90	18605·8	16·55	16·29	13·72	15·26	3441·8
200	5	20·50	18622·4	16·15	15·87	14·14	23·45	3445·2

The barometer (corrected to 32°) read 30·01 inches.

Experiment 7.—Globe G. Thermometers B and C. November 8, 1859.

Weight of water introduced $=3{\cdot}76+2{\cdot}373=6{\cdot}133$ grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr.°	Fahr.°	Fahr.°	inches.	inches.	inches.
12 35	209·5	209·5	262	17·75	4·88	12·87
12 41	209·5	209·5	265	17·75	4·88	12·87
1 0	190	190	263	18·30	4·88	13·42
1 5	190	190	268	18·27	4·88	13·39
1 12	190	190	268	18·27	4·88	13·39
1 22	186	186	268	18·42	4·88	13·54
1 30	186	186	260	18·42	4·88	13·54
1 40	182	182	262	18·66	4·88	13·78
1 46	182	182	260	18·66	4·88	13·78
1 50	182	182	260	18·66	4·88	13·78
2 10	178	178	270	19·70	4·88	14·82
2 15	178	178	270	19·61	4·88	14·73
2 20	178	178	270	19·68	4·88	14·80
2 27	178	178	260	19·72	4·88	14·84
2 40	181	181	265	18·95	4·88	14·07
2 45	181	181	265	18·97	4·88	14·09
2 50	181	181	263	18·90	4·88	14·02
3 0	182	182	265	18·76	4·88	13·88
3 10	183	183	263	18·77	4·88	13·89

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
178°	4	19·68	18644·5	14·80	14·61	14·80	14·66	3044·8
181	3	18·94	18672·2	14·06	13·85	15·58	15·60	3049·6
182	4	18·68	18680·7	13·88	13·67	15·82	15·90	3051·0
186	2	18·42	18689·3	13·54	13·33	16·01	17·44	3052·6
190	3	18·27	18694·3	13·40	13·20	16·14	18·99	3053·5
209·5	2	17·75	18712·4	12·87	12·65	16·67	28·57	3057·1

Experiment 8.—Globe G. Thermometers B and C. November 15, 1859.

Weight of water introduced $=5{\cdot}00+2{\cdot}15=7{\cdot}15$ grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr.°	Fahr.°	Fahr.°	inches.	inches.	inches.
11 45	211	211	226	15·85	4·47	11·38
11 51	211	211	228	15·85	4·47	11·38
11 55	211	211	226	15·82	4·47	11·35
11 58	211	211	227	15·80	4·47	11·33
12 0	211	211	227	15·80	4·47	11·33
12 15	191	191	224	16·40	4·47	11·93
12 20	191	191	223	16·41	4·47	11·94
12 25	191	191	228	16·39	4·47	11·92
12 28	191	191	228	16·41	4·47	11·94
12 30	191	191	228	16·41	4·47	11·94
12 40	186	186	225	17·35	4·47	12·88
12 45	186	186	227	17·35	4·47	12·88
12 48	186	186	227	17·30	4·47	12·83
12 52	186	186	225	17·25	4·47	12·78
12 55	186	186	228	17·30	4·47	12·83
12 57	186	186	228	17·23	4·47	12·76
6 0	186	186	227	17·26	4·47	12·79
1 10	181	181	227	19·28	4·46	14·82
1 15	181	181	226	19·16	4·46	14·70
1 18	181	181	226	19·18	4·46	14·72
1 20	181	181	226	19·18	4·46	14·72

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Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
181°	4	19·20	18660·7	14·74	14·52	15·61	15·60	2614·2
186	7	17·29	18727·0	12·82	12·62	17·51	17·44	2623·4
191	5	16·40	18756·5	11·93	11·75	18·38	19·43	2627·8
211	5	15·82	18775·7	11·35	11·16	18·97	29·42	2631·2

The barometer read 30·13 inches.

Experiment 9.—Globe G. Thermometers B and C. November 15, 1859.

Weight of water introduced = 7·15 + 1·648 = 8·798 grains.

Time.	Thermometers in water-bath.		Thermometer in mercury.	Cathetometer.		Difference of level of columns.
	B.	C.		Globe-stem.	Mercury-bath.	
h m	Fahr.	Fahr.	Fahr.	inches.	inches.	inches.
4 57	211	211	227	11·56	4·47	7·09
5 0	211	211	227	11·55	4·47	7·08
5 4	211	211	227	11·55	4·47	7·08
5 6	211	211	227	11·55	4·47	7·08
5 17	201	201	227	11·90	4·47	7·43
5 25	201	201	229	11·95	4·47	7·48
5 28	201	201	229	11·95	4·47	7·48
5 30	201	201	231	11·94	4·47	7·47
5 33	201	201	230	11·94	4·47	7·47
5 45	196	196	230	12·79	4·47	8·32
5 50	196	196	228	12·80	4·47	8·33
5 53	196	196	230	12·82	4·47	8·35
5 55	196	196	230	12·79	4·47	8·32
6 15	191	191	230	15·16	4·47	10·69
6 22	191	191	228	15·14	4·47	10·67
6 25	191	191	228	14·95	4·47	10·48
6 27	191	191	227	15·10	4·47	10·63
6 30	191	191	227	15·10	4·47	10·63

Summary of Column Determinations.

Temperature, Fahr.	Number of determinations averaged.	Mean level of column in globe-stem, in inches.	Capacity of globe, in grains of water at 39°·1.	Mean difference of level of columns, in inches.	Mean difference of level of columns, corrected to 32°, in inches.	Pressure of steam in globe, in inches of mercury.	Pressure of saturated steam, in inches of mercury.	Specific volume of steam in globe, corrected for expansion of glass.
191	5	15·09	18799·8	10·63	10·47	19·69	19·40	2140·6
196	4	12·80	18876·8	8·33	8·20	21·96	21·57	2149·5
201	5	11·94	18906·4	7·46	7·34	22·82	23·94	2152·9
211	4	11·55	18917·1	7·08	6·96	23·26	29·33	2154·5

The barometer read from 30·16 inches to 30·23 inches during this experiment.

Reduced by the same formulæ as before, we obtain the following general Table of Results of the experiments below the atmospheric pressure.

TABLE of Results reduced from preceding Experiments.

Number of experiment.	Maximum temperature of saturation, Fahrenheit.		Pressure, in inches of mercury.		Specific volume of steam.	Maximum temperature of saturation, Centigrade.	Pressure, in millimetres of mercury.
	°	°	inches.	°		°	°
1.	136·85 136·70	136·77	5·36 5·34	5·35	8275·3	58·20	135·9
2.	155·38 155·28	155·33	8·64 8·61	8·62	5333·5	68·51	218·9
3.	159·35 159·35 159·40	159·36	9·45 9·45 9·46	9·45	4920·2	70·75	240·0
4.	170·88 170·96	170·92	12·46 12·48	12·47	3722·6	77·18	316·7
5.	171·52 171·44	171·48	12·63 12·60	12·61	3715·1	77·49	320·3
6.	174·92		13·62		3438·1	79·40	346·0
7.	182·26 182·34	182·30	16·01 16·02	16·01	3051·0	83·50	406·7
8.	188·30		18·36		2623·4	86·83	466·4
9.	198·78		22·88		2149·5	92·65	581·1

SECTION III.—*Generalization of Results.*

As we purpose to extend these experiments to steam of very high pressure, and to institute a distinct series of experiments on the law of expansion of superheated steam, any elaborate generalizations of the results of the present series of experiments would be premature. In the mean time, however, we give the following general summary of results.

On the Relation of Specific Volume and Pressure of Saturated Steam.

Let V be the specific volume of a given weight of saturated steam, at the pressure P, measured by a column of mercury in inches; then

$$V = 25{\cdot}62 + \frac{49513}{P + {\cdot}72} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.)^*$$

and

$$P = \frac{49513}{V - 25{\cdot}62} - {\cdot}72 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.)$$

The following Table shows that formula (7.) represents with considerable accuracy the results of our experiments, and also that they are for the most part perfectly consistent with one another.

* These formulæ, expressed in French millimetres instead of English inches, would be

$$V = 25{\cdot}62 + \frac{1257605}{P + 18{\cdot}29} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10.)$$

$$P = \frac{1257605}{V - 25{\cdot}62} - 18{\cdot}29 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.)$$

TABLE showing the relation of Density, Pressure, and Temperature of Saturated Steam.

Number of experiment.	Pressure, in inches of mercury. P.	Maximum temperature of saturation. t.	Specific volume from experiment. V.	Specific volume from formula (7.). V.	Proportional error of formula (7.).
1.	5·35	136·77	8275·3	8183	$-\frac{1}{90}$
2.	8·62	155·33	5333·5	5326	$-\frac{1}{718}$
3.	9·45	159·36	4920·2	4900	$-\frac{1}{248}$
4.	12·47	170·92	3722·6	3766	$+\frac{1}{87}$
5.	12·61	171·48	3715·1	3740	$+\frac{1}{149}$
6.	13·62	174·92	3438·1	3478	$+\frac{1}{80}$
7.	16·01	182·30	3051·0	2985	$-\frac{1}{46}$
8.	18·36	188·30	2623·4	2620	$+\frac{1}{574}$
9.	22·88	198·78	2149·5	2124	$-\frac{1}{90}$
1′.	53·61	242·90	943·1	937	$-\frac{1}{157}$
2′.	55·52	244·82	908·0	906	$-\frac{1}{214}$
3′.	55·89	245·22	892·5	900	$+\frac{1}{111}$
4′.	66·84	255·50	759·4	758	$-\frac{1}{749}$
5′.	76·20	263·14	649·2	669	$+\frac{1}{38}$
6′.	81·53	267·21	635·3	628	$-\frac{1}{91}$
7′.	84·20	269·20	605·7	608	$+\frac{1}{304}$
8′.	92·23	274·76	584·4	562	$-\frac{1}{26}$
9′.	90·08	273·30	543·2	545	$+\frac{1}{211}$
10′.	99·60	279·42	515·0	519	$+\frac{1}{138}$
11′.	104·54	282·58	497·2	496	$-\frac{1}{497}$
12′.	112·78	287·25	458·3	461	$+\frac{1}{132}$
13′.	122·25	292·53	433·1	428	$-\frac{1}{56}$
14′.	114·25	288·25	449·6	456	$+\frac{1}{75}$

On the Law of Expansion of Superheated Steam.

Adopting the notation already employed, and putting r for the rate or coefficient of expansion of an elastic fluid at t_1 temperature, we find

$$r=\frac{1}{t_1+t_1}=\frac{\frac{V_2p_2}{V_1p_1}-1}{t_2-t_1}, \quad \ldots \ldots \ldots \ldots \quad (9.)$$

where $\frac{1}{t_1}$ represents the rate of expansion at zero of temperature. In the case of air $\frac{1}{t_1}=\frac{1}{459}$, so that at 212° the rate of expansion $r=\frac{1}{459+212}=\frac{1}{671}$, and so on to other cases.

This formula is strictly true for all perfectly elastic fluids such as air; and if the intervals (t_2-t_1) and (p_2-p_1) are small, it will give, with a near approach to truth, the rate of expansion of any imperfectly elastic fluid, such as superheated steam.

The following Table gives the value of the coefficient of expansion of superheated steam taken at different intervals of temperature from the maximum temperature of saturation.

TABLE showing the Coefficient of Expansion of Superheated Steam.

Number of experiment.	Maximum temperature of saturation.	Temperatures between which the expansion is taken.	Coefficient of expansion of steam.	Coefficient of expansion of air.
1.	136°·77	140° , 170°	$\frac{1}{250}$	$\frac{1}{500}$
2.	155·33	160 , 190	$\frac{1}{218}$	$\frac{1}{487}$
3.	159·36	159·36, 170·2	$\frac{1}{150}$	$\frac{1}{615}$
		170·2 , 209·9	$\frac{1}{614}$	$\frac{1}{619}$
5.	171·48	171·48, 180	$\frac{1}{320}$	$\frac{1}{630}$
		180 , 200	$\frac{1}{604}$	$\frac{1}{633}$
6.	174·92	174·92, 180	$\frac{1}{150}$	$\frac{1}{634}$
		180 , 200	$\frac{1}{617}$	$\frac{1}{638}$
7.	182·30	182·3 , 186	$\frac{1}{230}$	$\frac{1}{617}$
		186 , 209·5	$\frac{1}{610}$	$\frac{1}{618}$
8.	188·30	191 , 211	$\frac{1}{604}$	$\frac{1}{610}$
1′.	242·9	243 , 249	$\frac{1}{217}$	$\frac{1}{703}$
4′.	255·5	257 , 259	$\frac{1}{303}$	$\frac{1}{718}$
		257 , 264	$\frac{1}{600}$	$\frac{1}{716}$
6′.	267·21	268 , 271	$\frac{1}{310}$	$\frac{1}{737}$
		271 , 279	$\frac{1}{610}$	$\frac{1}{730}$
7′.	269·2	271 , 273	$\frac{1}{233}$	$\frac{1}{730}$
		273 , 279	$\frac{1}{581}$	$\frac{1}{733}$
9′.	279·42	283 , 285	$\frac{1}{205}$	$\frac{1}{712}$
		285 , 289	$\frac{1}{533}$	$\frac{1}{714}$
13′.	292·53	297 , 299	$\frac{1}{281}$	$\frac{1}{716}$
		299 , 302	$\frac{1}{633}$	$\frac{1}{716}$

The results recorded in this Table distinctly show that, for temperatures within about ten degrees from the maximum temperature of saturation, the rate of expansion greatly exceeds that of air, whereas at higher temperatures from this point the rate of expansion approaches that of air; thus, for example, in Experiment 6, between the temperatures of 174°·92 and 180°, the coefficient of expansion is $\frac{1}{150}$, that is, about three times that of air; whereas between the temperatures of 180° and 200° the coefficient of expansion is very nearly the same as that of air, and so on in other cases. At temperatures somewhat removed from the maximum temperature of saturation, the coefficient of expansion in the high-pressure experiments is decidedly greater than that of air, whereas in the low-pressure experiments it does not greatly differ from that of air. The mean of ϵ_1 in the latter case $=\frac{1}{7}(453+406+467+424+457+444+413)=438$, whilst for air this constant is 459.

Hence it appears that, as the steam becomes more and more superheated, the coefficient of expansion approaches that of a perfect gas, but that at and near to the maximum temperature of saturation the coefficient of expansion greatly exceeds that of a perfect gas.

Explanation of the Plates.

PLATE VII.

Represents the apparatus for the experiments on the density of steam detailed in Section I.

Fig. 1. Elevation showing the general arrangement of the apparatus, the copper boiler B, gauge G, thermometer t, oil-bath C, inner and outer tubes forming the saturation-gauge o, i, cathetometer ff.

Fig. 2. A corresponding vertical section, and

Fig. 3. A plan.

PLATE VIII.

Fig. 1. Represents the apparatus for the experiments in Section II., shown in a vertical section: B copper boiler, t, t' thermometers, A the globe of glass containing the weighed portion of water, C the lower mercury-bath, x double-pointed pin for reading the lower mercury level, h lamp, and e, e gas-jets.

Fig. 2. Represents the cathetometer with its vernier and telescope.

Fig. 3. Represents the vernier and thumbscrew of the cathetometer seen on the other side.

Fig. 4. The glass globe, after the formation of the Torricellian vacuum, arranged with its cap k, supported by an india-rubber band for insertion in the boiler for one of the experiments at the higher pressures.

Fig. 5. A section of the cap and globe-stem of fig. 4, showing the platinum wire, &c.

Fig. 6. Different-sized globules for containing weighed portions of water.

Fig. 7. Cup and filled globule ready for transference to the glass globe.

Fig. 8. Bottom of the globe-stem arranged for a transference to the boiler for a low-pressure experiment; the india-rubber cap c is removed during the experiment.

PLATE IX.

A diagram in which the relation of temperature and specific volume of steam is represented in a curve, the ordinates of which represent the increments of temperature, and the abscissæ the increments of specific volume: the marks (×) indicate points determined experimentally, and the three curves the relations of specific volume and temperature as given by the common formula derived from the gaseous laws, by Mr. Rankine's formula, and by formula (7.), page 219, of this paper derived from our experiments.

XIII. *On a new Method of Approximation applicable to Elliptic and Ultra-elliptic Functions.* By CHARLES W. MERRIFIELD. *Communicated by the Rev.* H. MOSELEY, *F.R.S.*

Received March 26,—Read May 24, 1860.

THE difficulty of finding approximate values of elliptic functions of the third kind has led me to consider a general method of approximation, which I believe to be new, at least in its application to the evaluation of integrals of irrational functions.

It depends on the known principle that the geometric mean between two quantities is also a geometric mean between their arithmetic and harmonic means. If we take any two positive quantities, we may approximate to their geometric means as follows:—Take the arithmetic and harmonic means of the two quantities, then again take the arithmetic and harmonic means of those means, and so on: the successive means will approximate with great rapidity to the geometric mean.

To judge of the convergence of the method, I give, in the first two columns of the following little Table, the arithmetic and harmonic means thus derived from the numbers 1 and 2 (which is the most unfavourable case that need present itself). The third column contains the difference of the first two, within which lies the error of either.

$\frac{3}{2}$	$\frac{4}{3}$	$\frac{1}{6}$
$\frac{17}{12}$	$\frac{24}{17}$	$\frac{1}{204}$
$\frac{577}{408}$	$\frac{816}{577}$	$\frac{1}{235416}$
$\frac{665857}{470832}$	$\frac{941664}{665857}$	$\frac{1}{313506783024}$

Either of the fourth pair would thus give the square root of 2, correct to eleven places of decimals.

This method finds its application in evaluating the integral $\int fx.\sqrt{\phi x}.dx$, where fx and ϕx are rational functions of x which both increase or decrease regularly, and have no singular values, within the limits of integration. If we find successive means, as above described, say A_n and H_n, between fx and $fx.\phi x$, then it is clear that, since $fx\sqrt{\phi x}$ always lies between A_n and H_n, so $\int fx.\sqrt{\phi x}.dx$ must lie between $\int A_n.dx$ and $\int H_n.dx$. Now A_n and H_n are each the product of fx and a rational function of ϕx, and are therefore themselves rational functions of x. They are therefore always integrable.

It is not to be denied that the application of this method to the functions which call

for its use is cumbrous; but there is no other way of treating them which is not open to the same complaint, for, in reality, they are exceedingly complex of themselves.

The following are the first three terms of the arithmetic means, with the corresponding harmonic means written under them, derived from x and y:—

$$\frac{x+y}{2}, \qquad \frac{x^2+6xy+y^2}{4(x+y)}, \qquad \frac{x^4+28x^3y+70x^2y^2+28xy^3+y^4}{8(x^3+7x^2y+7xy^2+y^3)},$$

$$\frac{2xy}{x+y}, \qquad \frac{4xy(x+y)}{x^2+6xy+y^2}, \qquad \frac{8xy(x^3+7x^2y+7xy^2+y^3)}{x^4+28x^3y+70x^2y^2+28xy^3+y^4}.$$

It is convenient to use the arithmetic in preference to the harmonic series for integration, as the divisor contains one binomial factor less. The third arithmetic mean may be resolved into the following form:—

$$\frac{x+y}{8}+\frac{1}{2}\frac{xy}{x+y}+\frac{1}{2}\frac{(2+\sqrt{2})xy}{x+(3+2\sqrt{2})y}+\frac{1}{2}\frac{(2-\sqrt{2})xy}{x+(3-2\sqrt{2})y}.$$

Note that

$$(2+\sqrt{2})^3=2(3+2\sqrt{2})=\frac{2}{3-2\sqrt{2}}=\frac{4}{(2-\sqrt{2})^3},$$

and that

$$\log(3+2\sqrt{2})=0{\cdot}76555\ \ 13706\ \ 75726.$$

If a further approximation be thought necessary, it is possible to resolve into partial fractions the fourth arithmetic mean; but if we go beyond this we shall have to solve a reciprocal equation of the eighth degree with all its roots real. The fourth arithmetic mean will have for its divisor

$$16(x+y)(x^3+6xy+y^3)(x^4+28x^3y+70x^2y^2+28xy^3+y^4):$$

the roots of the biquadratic factor, with their signs changed, are

$$7\pm4\sqrt{2}+\sqrt{(80\pm56\sqrt{2})} \text{ and } 7\pm4\sqrt{2}-\sqrt{(80\pm56\sqrt{2})}:$$

their approximate values are

25·27414	23690	882
2·23982	88088	434
0·44646	26921	718
0·03956	61298	966

The difference between any (say the nth) pair of means of the series has always $(x-y)$ to the power of 2^n for its numerator, and the product of the denominators for its denominator. The logarithm of the error is therefore always much less than

$$2^n\log(x-y)-(2^n-1)\log(x+y)-n\log 2.$$

I shall now indicate the mode of applying this method to the general form of an elliptic function, $\int\frac{1+N\sin^2\varphi}{1+n\sin^2\varphi}\frac{d\varphi}{\sqrt{1-c^2\sin^2\varphi}}=\int u\,d\varphi$.

It is obvious that the nearer the ratio $x:y$ is to unity, the less number of terms shall we require to obtain a given degree of accuracy. In elliptic functions which involve a

radical of the form $\sqrt{1-c^2\sin^2\varphi}$, this ratio may always be brought within the limits of $\frac{1}{2}$ and $\frac{2}{1}$; for, if $c\sin\varphi$ should exceed $\frac{1}{\sqrt{2}}$, we may put the radical under one of the forms $\cos\varphi\sqrt{1+(1-c^2)\tan^2\varphi}$ or $\sqrt{1-c^2}\sqrt{1+\frac{c^2}{1-c^2}\tan^2\varphi}$, and one or other of these new radicals will always be less than $\sqrt{2}$. I should have remarked that c never exceeds unity.

We may take u as a geometrical mean between v and $v(1-c^2\sin^2\varphi)$, where

$$v=\frac{1+N\sin^2\varphi}{(1+n\sin^2\varphi)(1-c^2\sin^2\varphi)}=\frac{c^2+N}{c^2+n}\,\frac{1}{1-c^2\sin^2\varphi}+\frac{n-N}{c^2+n}\,\frac{1}{1+n\sin^2\varphi}.$$

We can put $x=1$ and $y=1-c^2\sin^2\varphi$, or *vice versâ*, as may be convenient. Making either substitution, and reducing to partial fractions the mean which we select for integration, we have to multiply each fraction by the second value of v, which doubles the number of fractions, and the index of their denominators; but on again decomposing the fractions, and grouping them by their denominators, we reduce them to two more than those into which we had previously decomposed the mean. The two extra fractions will, of course, have $1+n\sin^2\varphi$ and $1-c^2\sin^2\varphi$ for their denominators. If we stop at the third arithmetic mean we shall thus have five partial fractions to integrate, and for the third harmonic mean, six. I do not actually exhibit the work or its results, because my doing so would not save labour to any one. Not only would the resulting formula be complicated with constants more easily managed in an arithmetical form, but it will seldom happen in practice that it will be worth while to reduce the elliptic function to the normal form given above. I have, however, done enough to show that my method is capable of approximately reducing any form, containing a function under the radical of the square root, to a small series of terms involving, at highest, logarithms or inverse tangents in their integrals. Moreover the approximation is so rapid, that, in the case of an elliptic integral of the third kind and of logarithmic form, nothing would be gained by having recourse to the interpolation of the only possible table, that of the double integral $\int_0^\theta \frac{1}{\sqrt{1-c^2\sin^2\theta}}\int_0^\theta\sqrt{1-c^2\sin^2\theta}.d\theta^2$. The third pair of means will give six or more places of figures correct, and the fourth arithmetic mean is capable of giving twelve places.

With respect to the actual integration of the partial fractions ultimately obtained, there is no difficulty. It will easily be seen that each partial fraction will be of the form $\frac{a}{1+p\sin^2\varphi}$. The integral of this with regard to φ is

$$\frac{1}{\sqrt{1+p}}\tan^{-1}\{\sqrt{1+p}.\tan\varphi\}.$$

If $1+p$ is negative ($=-q^2$, suppose), this integral takes the form

$$\frac{1}{2q}\log_e\left\{\frac{1+q\tan\varphi}{1-q\tan\varphi}\right\}.$$

It is obvious that we may approximate in the same way to the values of ultra-elliptic integrals; but the process will be more lengthy, on account of the greater complexity of these functions.

In the case of higher radicals than the square root, so far as concerns a first approximation only, it is clear that, if we insert several means between two integrable functions, any given geometric mean will be intermediate in value to the corresponding arithmetic and harmonic means; but, inasmuch as the process affords no indication of what the second step is to be, it does not seem to have any useful application to such functions. But it brings *all* elliptic and ultra-elliptic functions within practical reach of the numerical computer.

ADDENDUM.

Received March 29,—Read May 24, 1860.

I have thought it advisable, upon reconsideration, to give the approximate formula for $\int_0^\varphi \frac{1+N\sin^2\varphi}{1+n\sin^2\varphi}\frac{d\varphi}{\sqrt{1-c^2\sin^2\varphi}}$ derived from the third mean of the arithmetic series:—

$$\frac{1}{8}\frac{N}{n}\varphi+\left\{\frac{1}{8}+\frac{1}{8}\frac{1}{n+c^2}+\frac{1}{4}\frac{1}{n+\frac{1}{2}c^2}+\frac{1}{4}\frac{1}{n+\frac{2+\sqrt{2}}{4}c^2}+\frac{1}{4}\frac{1}{n+\frac{2-\sqrt{2}}{4}c^2}\right\}\frac{n-N}{\sqrt{1+n}}\tan^{-1}\{(1+n)^{\frac{1}{2}}.\tan\varphi\}$$

$$+\frac{1}{8}\frac{N+c^2}{n+c^2}\frac{1}{\sqrt{1-c^2}}\tan^{-1}\{(1-c^2)^{\frac{1}{2}}.\tan\varphi\}+\frac{1}{4}\frac{N+\frac{1}{2}c^2}{n+\frac{1}{2}c^2}\left(1-\frac{1}{2}c^2\right)^{-\frac{1}{2}}\tan^{-1}\left\{\left(1-\frac{1}{2}c^2\right)^{\frac{1}{2}}\tan\varphi\right\}$$

$$+\frac{1}{4}\frac{N+\frac{2+\sqrt{2}}{4}c^2}{n+\frac{2+\sqrt{2}}{4}c^2}\left(1-\frac{2+\sqrt{2}}{4}c^2\right)^{-\frac{1}{2}}\tan^{-1}\left\{\left(1-\frac{2+\sqrt{2}}{4}c^2\right)^{\frac{1}{2}}\tan\varphi\right\}$$

$$+\frac{1}{4}\frac{N+\frac{2-\sqrt{2}}{4}c^2}{n+\frac{2-\sqrt{2}}{4}c^2}\left(1-\frac{2-\sqrt{2}}{4}c^2\right)^{-\frac{1}{2}}\tan^{-1}\left\{\left(1-\frac{2-\sqrt{2}}{4}c^2\right)^{\frac{1}{2}}\tan\varphi\right\}.$$

I also observe that com. $\log\frac{2+\sqrt{2}}{4}=9{\cdot}93123\ 06918\ 42$

$$\log\frac{2-\sqrt{2}}{4}=9{\cdot}16567\ 93211\ 66.$$

The application of this formula, in the shape given above, requires that $1+n$ be positive, and that $c\sin\varphi$ shall not exceed $\sin 45°$.

If we equate n to N, we obtain for the approximate value of $\int_0^{\varphi}(1-c^2\sin^2\varphi)^{-\frac{1}{2}}d\varphi$, or $F(c\varphi)$,

$$\frac{1}{8}\varphi+\frac{1}{8}(1-c^2)^{-\frac{1}{2}}\tan^{-1}\{(1-c^2)^{\frac{1}{2}}\tan\varphi\}+\frac{1}{4}\left(1-\frac{1}{2}c^2\right)^{-\frac{1}{2}}\tan^{-1}\left\{\left(1-\frac{1}{2}c^2\right)^{\frac{1}{2}}\tan\varphi\right\}$$
$$+\frac{1}{4}\left\{1-\frac{2+\sqrt{2}}{4}c^2\right\}^{-\frac{1}{2}}\tan^{-1}\left\{\left(1-\frac{2+\sqrt{2}}{4}c^2\right)^{\frac{1}{2}}\tan\varphi\right\}$$
$$+\frac{1}{4}\left\{1-\frac{2-\sqrt{2}}{4}c^2\right\}^{-\frac{1}{2}}\tan^{-1}\left\{\left(1-\frac{2-\sqrt{2}}{4}c^2\right)^{\frac{1}{2}}\tan\varphi\right\}$$

I now apply the numerical values $\varphi=\frac{1}{2}\pi$, $c=\sin 45°$, which, as has already appeared, lead to the most unfavourable case for approximation. For $\varphi=\frac{1}{2}\pi$ all the inverse tangents become $=\frac{1}{2}\pi$, and, by reducing the last two terms to a single radical, we easily obtain

$$F\left(\sin 45°, \tfrac{1}{2}\pi\right)=\tfrac{1}{2}\pi\left\{\tfrac{1}{8}+\tfrac{1}{4}\sin 45°+\tfrac{1}{8}\sin 60°+\sqrt{\frac{6+\sqrt{34}}{34}}\right\}$$
$$=\tfrac{1}{2}\pi\times 1{\cdot}18034\ 09494\ 53=1{\cdot}85407\ 52150.$$

This exceeds the exact value given by LEGENDRE, 1·85407 46773, by 0·00000 05377. The logarithm of the factor of $\frac{1}{2}\pi$ is 0·07200 74743, of which the error is 0·00000 01290, in excess.

It follows from this that the necessary error of the process, where the third mean of the arithmetic series is used, will never be more than a unit in the seventh place, and it is evident that this error will always be in excess. By an arbitrary correction, of which the amount may be easily guessed in any given case, the seventh place may always be made accurate.

XIV. *On Quaternary Cubics.* *By the Rev.* GEORGE SALMON, *D.D., M.R.I.A.*

Communicated by A. CAYLEY, *Esq.*

Received June 14,—Read June 21, 1860.

IN the following memoir I propose to make an attempt at an enumeration of the invariants, covariants, and contravariants of a quaternary cubic, that is to say, of a homogeneous function of the third order in four variables, which geometrically represents a surface of the third order. This memoir, then, will be in continuation of Mr. CAYLEY'S memoirs on Quantics, wherein a similar analysis is very completely performed for binary quantics as far as the fifth order, and for ternary quantics as far as the third order.

In consequence of the great length of the formulæ when the general equation is used, I work with Mr. SYLVESTER'S canonical form

$$U = ax^3 + by^3 + cz^3 + dw^3 + ev^3,$$

where the variables are connected by the relation

$$x + y + z + u + v = 0.$$

It will be found that the discussion of this form leads to some results resembling those obtained for binary quantics of the fifth order; the one quantic being canonically expressed as the sum of five third powers, the other as the sum of three fifth powers.

Mr. SYLVESTER has calculated the Hessian of a cubic expressed in the form given above, but in order to obtain with facility new covariants, it is desirable that we should also be in possession of a contravariant. We should then be able to substitute differential symbols for the contragredient variables, and should thus have an operating symbol by the help of which we could derive new covariants from those known already.

Let, then, α, β, γ, δ, ϵ be contragredient variables; let us suppose that when the original function U is expressed in terms of four independent variables, we have got any contravariant in α, β, γ, δ; and let us consider what this will become when the function U is expressed in terms of five variables connected by a linear relation. Now the contravariant in question expresses geometrically the condition that the plane $\alpha x + \beta y + \gamma z + \delta u + \epsilon v$ should possess a certain connexion with the surface represented by U. This plane, expressed in terms of four variables, is

$$(\alpha - \epsilon)x + (\beta - \epsilon)y + (\gamma - \epsilon)z + (\delta - \epsilon)u;$$

and it is apparent that the contravariant in terms of five letters is derived from that expressed in terms of four letters, by substituting $\alpha - \epsilon$, $\beta - \epsilon$, $\gamma - \epsilon$, $\delta - \epsilon$ respectively for

$\alpha, \beta, \gamma, \delta$. Every contravariant, then, in five letters will be a function of the differences between $\alpha, \beta, \gamma, \delta, \varepsilon$.

It is easy to show now that $\alpha, \beta, \gamma, \delta, \varepsilon$ are cogredient with $\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}, \frac{d}{du}, \frac{d}{dv}$ respectively. We know, in fact, that when U is expressed in terms of four letters, we may substitute in any contravariant, for $\alpha, \beta, \gamma, \delta$, $\frac{d}{dx}, \frac{d}{dy}, \frac{d}{dz}, \frac{d}{du}$. When, then, U is transformed into a function of five letters, we must substitute for $\frac{d}{dx}$, $\frac{d}{dx}+\frac{d}{dv}\frac{dv}{dx}$, which (in virtue of the relation connecting x, y, z, u, v) is equal to $\frac{d}{dx}-\frac{d}{dv}$; and similarly for $\frac{d}{dy}$, &c. But these are the very transformations by which the contravariant in four letters is expressed in terms of five.

It is equally easy to show that in a covariant we may substitute for x, y, z, u, v, $\frac{d}{d\alpha}, \frac{d}{d\beta}, \frac{d}{d\gamma}, \frac{d}{d\varepsilon}, \frac{d}{d\iota}$.

Let us commence by applying these principles to calculate the discriminant and reciprocant of a quaternary quadric when expressed in the form

$$ax^2+by^2+cz^2+du^2+ev^2.$$

These functions are known when the quadric is expressed in the general form

$$ax^2+by^2+cz^2+du^2 \\ +2lyz+2mzx+2nxy+2pxu+2qyu+2rzu.$$

In this case the discriminant is—

(No. 1.)

$$abcd-(adl^2+bdm^2+cdn^2+bcp^2+caq^2+abr^2) \\ +2(alqr+bmpr+cnpq+dlmn) \\ +l^2p^2+m^2q^2+n^2r^2-2mnqr-2nlrp-2lmpq.$$

The reciprocant (which is also called the bordered Hessian, since it is obtained by bordering with contragredient variables the determinant which expresses the Hessian) is—

(No. 2.)

$$\alpha^2(bcd-br^2-cq^2-dl^2+2lqr) \\ +\beta^2(cda-cp^2-dm^2-ar^2+2pmr) \\ +\gamma^2(dab-dn^2-aq^2-bp^2+2nqp) \\ +\delta^2(abc-al^2-bm^2-cn^2+2lmn) \\ +2\beta\gamma(-adl+aqr+dmn+lp^2-nrp-mpq) \\ +2\gamma\alpha(-bdm+bpr+dln+mq^2-nqr-lpq) \\ +2\alpha\beta(-cdn+cpq+dlm+nr^2-mqr-lrp) \\ +2\alpha\delta(-bcp+bmr+cnq+l^2p-nlr-lmq) \\ +2\beta\delta(-caq+alr+cnp+m^2q-mnr-lmp) \\ +2\gamma\delta(-abr+alq+bmp+n^2r-mnq-nlp).$$

Let us now examine what the latter function becomes when the given quantic is in the form

$$ax^3+by^3+cz^3+du^3+ev^3.$$

Eliminating v by the help of the relation connecting x, y, z, u, v, the coefficients of x^3, y^3, z^3, u^3 become $a+e$, $b+e$, $c+e$, $d+e$ respectively, while every other coefficient becomes e. Substituting these values in No. 2, the contravariant is

$$\begin{aligned}&\alpha^2\{bcd+(bc+cd+db)e\}\\+&\beta^2\{cda+(da+ac+cd)e\}\\+&\gamma^2\{dab+(ab+bd+da)e\}\\+&\delta^2\{abc+(bc+ca+ab)e\}\\-&2e\{ad\beta\gamma+bd\gamma\alpha+cd\alpha\beta+bc\alpha\delta+ca\beta\delta+ab\gamma\delta\}.\end{aligned}$$

Lastly, write in the form just found $\alpha-\varepsilon$, $\beta-\varepsilon$, $\gamma-\varepsilon$, $\delta-\varepsilon$ for α, β, γ, δ, and it becomes

$$\begin{aligned}&bcd(\alpha-\varepsilon)^2+cda(\beta-\varepsilon)^2+dab(\gamma-\varepsilon)^2+abc(\delta-\varepsilon)^2+bce(\alpha-\delta)^2+cae(\beta-\delta)^2\\&+abe(\gamma-\delta)^2+ade(\beta-\gamma)^2+bde(\alpha-\gamma)^2+cde(\alpha-\beta)^2,\end{aligned}$$

or, as it may be written, (No. 2 bis)

$$\Sigma cde(\alpha-\beta)^2.$$

I have given this work at length, in order fully to illustrate the process employed in other cases. The discriminant may be obtained either by substituting in No. 1, $a+e$, $b+e$, $c+e$, $d+e$ for a, b, c, d, or by substituting in No. 2 bis, differential symbols for α, β, γ, δ, ε, and operating on U. In either case we get—

(No. 1 bis)

$$bcde+cdea+deab+eabc+abcd,$$

or

$$\Sigma abcd.$$

If the given quadric had been given as a function in its most general form of five variables connected by the relation $x+y+z+u+v$, its discriminant would have been got by taking the bordered Hessian of the quadric (the variables being considered as independent), and then writing $\alpha=\beta=\gamma=\delta=\varepsilon=1$. And in general it is evident that any invariant of a function of n variables connected by the relation

$$\alpha x+\beta y+\gamma z+\delta u+\varepsilon v+\&c.=0,$$

is a contravariant of the same form considered as a function of n independent variables, α, β, γ, &c. being the contragredient variables.

The reciprocant and discriminant are the only functions concomitant to a quadric. Let us proceed, then, to the quaternary cubic

$$U=ax^3+by^3+cz^3+du^3+ev^3.$$

Its Hessian is the discriminant of any polar quadric,

$$axx'^2+byy'^2+czz'^2+duu'^2+evv'^2,$$

therefore, by No. 1 bis, is immediately, as Mr. SYLVESTER has also proved,

$$bcdeyzuv+cdeazuvx+deabuvxy+eabcvxyz+abcdxyzu,$$

or

$$\Sigma abcdxyzu.$$

We also get immediately from No. 2 bis a mixed concomitant, viz. the bordered Hessian, which may be written

$$\Sigma cdezuv(\alpha-\beta)^3.$$

If in this last we substitute differentials for α, β, &c. and operate on U, we get the Hessian. If we operate on the Hessian, we get a covariant of the fifth order, to which I shall afterwards refer as Φ,

$$\Phi=abcde\Sigma abx^2y^2z.$$

The reciprocant of the given quantic being, as is known, of the form $64S^3=T^2$, presents us with two other contravariants, S and T, the consideration of which is very fertile in results. If the quantic were to reduce itself to the form

$$ax^3+by^3+cz^3+du^3,$$

it is easy to see that the reciprocant reduces to

$$64(abcd\alpha\beta\gamma\delta)^3=\{\Sigma b^3c^3d^3\alpha^6-2\Sigma abc^3d^3\alpha^3\beta^3\}^2.$$

From this, then, we can readily anticipate the form of S in the general case, which, however, I have verified independently. It is of the fourth order in the variables and in the letters, and is

$$S=\Sigma abcd(\alpha-\varepsilon)(\beta-\varepsilon)(\gamma-\varepsilon)(\delta-\varepsilon);$$

that is to say,

$$\begin{aligned}&bcde(\alpha-\beta)(\alpha-\gamma)(\alpha-\delta)(\alpha-\varepsilon)+cdea(\beta-\alpha)(\beta-\gamma)(\beta-\delta)(\beta-\varepsilon)\\&+deab(\gamma-\alpha)(\gamma-\beta)(\gamma-\delta)(\gamma-\varepsilon)+eabc(\delta-\alpha)(\delta-\beta)(\delta-\gamma)(\delta-\varepsilon)\\&+abcd(\varepsilon-\alpha)(\varepsilon-\beta)(\varepsilon-\gamma)(\varepsilon-\delta).\end{aligned}$$

From this we can derive several other concomitant functions. For instance, operating on this with U, we expect to get a contravariant of the first degree in the variables, and the fifth in the coefficients, but this will be found to vanish identically. Operating with S on the Hessian, we get the simplest invariant of the cubic, to which I shall refer as Invariant A,

$$A=\Sigma b^3c^3d^3e^3-2abcde\Sigma abc.$$

Symbolically A is $(1235)(1246)(1347)(2348)(5678)^3$.

Again, operating with S on U^2, we get the simplest covariant quadric which is of the sixth order in the coefficients, and is

$$abcde(ax^3+by^3+cz^3+du^3+ev^3).$$

Symbolically this covariant is expressed $(1234)(1235)(1456)(2456)$. Again operating with this on S, we get a contravariant quadric of the tenth order in the coefficients; and

again operating with this last on U, we obtain a covariant of the first order in the variables and the eleventh in the coefficients. But it being sufficiently obvious that new invariants, covariants, and contravariants can be formed *ad libitum* by the process already explained of combining a covariant and contravariant already found, I consider it needless to enter into further detail as to the steps by which particular covariants are obtained, and proceed to form into tables the most important results.

I write, for brevity,

$$a+b+c+d+e=p,$$
$$ab+ac+ad+ae+bc+bd+be+cd+ce+de=q,$$
$$cde+bde+bce+bcd+ade+ace+acd+abe+abd+abc=r,$$
$$bcde+cdea+deab+eabc+abcd=s,$$
$$abcde=t.$$

I commence with the invariants of the cubic, which appear to be all reducible to the five following fundamental invariants of the 8th, 16th, 24th, 32nd, and 40th orders respectively:—

$$A=s^3-4rt.$$
$$B=t^3p.$$
$$C=t^4s.$$
$$D=t^6q.$$
$$E=t^8.$$

Whence also $C^2-AE=4t^8r$.

Since any invariant must be a symmetric function of a, b, c, d, e, it can be expressed in terms of p, q, r, s, t, and therefore in terms of A, B, C, D, E. We can form, however, precisely as in the case of binary quintics, skew invariants which cannot be expressed rationally in terms of the five fundamental invariants, but whose squares can be expressed as rational functions of these quantities. The simplest invariant of this kind is of the hundredth degree in the coefficients, and for the canonical form is t^{16} multiplied by the product of all the differences between any two of the quantities a, b, c, d, e. The following is the expression for the square of this invariant F in terms of the simpler invariants:—

$$\begin{aligned}256F^2=&\,800000\,E^5+240000\,E^4DA-640000\,E^4CB+36000\,E^4CA^2-128000\,E^4B^2A\\&+3600\,E^4BA^3-27\,E^4A^5+576000\,E^3D^2B+13200\,E^3D^2A^2+272000\,E^3DC^2\\&+131200\,E^3DCBA+2520\,E^3DCA^3-409600\,E^3DB^2+8960\,E^3DB^2A^2-72\,E^3DBA^4\\&+30400\,E^3C^2A+115200\,E^2C^2B^2+5520\,E^2C^2BA^2+108\,E^2C^2A^4-10240\,E^2CB^2A\\&-96\,E^2CB^2A^4+65536\,E^2B^4-2048\,E^2B^4A^2+16\,E^2B^2A^4-230400\,E^2D^2C\\&+40960\,E^2D^2AB-64\,E^2D^2A^3-62240\,E^2D^2C^2A+261120\,E^2D^2CB^2\\&+5696\,E^2D^2CBA^2-90240\,E^2DC^2B-9216\,E^2D^2B^2A+16\,E^2D^2B^2A^3-5256\,E^2DC^2A^3\end{aligned}$$

$$+29824\,E^7DC^3B^3A+216\,E^7DC^3BA^3-49152\,E^7DCB^4-1280\,E^7DCB^2A^3-864\,E^6C^4$$
$$-9552\,E^6C^4BA-162\,E^6C^4A^3+192\,E^5C^3B^3A^3+1024\,E^5C^3B^3-5120\,E^5C^3B^4A$$
$$-48\,E^4C^2B^3A^3+27648\,ED^4-6912\,ED^4B^3+4608\,ED^4CA-34816\,ED^3C^3B$$
$$+128\,ED^3C^3A^3-1152\,ED^3CB^3A+16272\,ED^3C^4-6272\,ED^2C^3BA+7680ED^2C^3B^3$$
$$+2952\,EDC^5A-32\,ED^2C^3B^3A^3-1920\,EDC^4B^3-216\,EDC^4BA^3+1408\,EDC^3B^3A$$
$$+432\,EC^6B+108\,EC^6A^3-96\,EC^5B^3A+256\,EC^4B^4+48\,EC^4B^2A^3-512\,D^4C^3$$
$$-64\,D^3C^4A+128\,D^3C^3B^3+576\,D^2C^3B+16D^2C^4B^3A+72\,DC^6BA-128\,DC^5B^3$$
$$-216\,DC^7-27\,C^8A-16\,C^6B^3A.$$

I next proceed to show how the discriminant of the surface is expressed in terms of the fundamental invariants A, B, C, D. And it will throw some light on the investigation if I first give the solution of the corresponding problem for a ternary cubic expressed in the form

$$ax^3+by^3+cz^3+du^3, \text{ where } x+y+z+u=0.$$

The following is a Table of the principal concomitants of this form:—

ARONHOLD's invariants:

$$S=abcd,$$

$$T=a^3b^3c^3+b^3c^3d^3+c^3d^3a^3+d^3a^3b^3-2abcd(ab+ac+ad+bc+cd+db).$$

The Hessian:

$$H=bcdyzu+cdazux+dabuxy+abcxyz.$$

It is obvious that the points xy, zu; xz, yu; xu, yz are pairs of corresponding points on the Hessian. The evectant of S, which Mr. CAYLEY calls the Pippian, is

$$bcd(\alpha-\beta)(\alpha-\gamma)(\alpha-\delta)+cda(\beta-\alpha)(\beta-\gamma)(\beta-\delta)+dab(\gamma-\alpha)(\gamma-\beta)(\gamma-\delta)$$
$$+abc(\delta-\alpha)(\delta-\beta)(\delta-\gamma),$$

from which form it can easily be deduced that the lines joining corresponding points on the Hessian touch the curve represented by this evectant, as do also the two lines into which the polar conic of any point on the Hessian breaks up.

The first evectant of T (called by Mr. CAYLEY the Quippian) is

$$\Sigma c^3d^3(a-b)(\alpha-\beta)^3-\Sigma d^3abc(2\alpha-\beta-\gamma)(2\beta-\gamma-\alpha)(2\gamma-\alpha-\beta);$$

and the second evectant of T, that is to say the Reciprocant, is

$$\Sigma c^3d^3(\alpha-\beta)^6-2\Sigma d^3bc(\alpha-\beta)^3(\alpha-\gamma)^3$$
$$+2abcd\{(\alpha-\gamma)(\beta-\delta)-(\alpha-\delta)(\gamma-\beta)\}\{(\alpha-\delta)(\gamma-\beta)-(\alpha-\beta)(\delta-\gamma)\}$$
$$\{(\alpha-\beta)(\delta-\gamma)-(\alpha-\gamma)(\beta-\delta)\}.$$

To return now to the problem of finding the discriminant of this plane cubic. This is obtained by eliminating the variables between the three polar conics got by differentiating the equation with regard to x, y, z respectively; viz.

$$ax^3-du^3, \quad by^3-du^3, \quad cz^3-du^3.$$

Each of these breaks up into factors: choosing any set of these factors, the resultant of the four factors comes out easily in the form of the determinant

$$\begin{vmatrix} \sqrt{a}+\sqrt{d}, & \sqrt{d} & , & \sqrt{d} \\ \sqrt{d}, & \sqrt{b}+\sqrt{d}, & & \sqrt{d} \\ \sqrt{d}, & \sqrt{d} & , & \sqrt{e}+\sqrt{d}; \end{vmatrix}$$

that is to say,

$$\sqrt{bcd}+\sqrt{cda}+\sqrt{dab}+\sqrt{abc}.$$

We are then to multiply together the eight results obtained by giving all possible variations of signs to the radicals, and the product will evidently be the same as the result of clearing of radicals the equation

$$\sqrt{bcd}+\sqrt{cda}+\sqrt{dab}+\sqrt{abc}=0;$$

that is to say,

$$\{b^2c^2d^2+c^2d^2e^2+d^2a^2b^2+a^2b^2c^2-2abcd(ab+ac+ad+bc+cd+db)\}^2=64a^3b^3c^3d^3,$$

or

$$T^2=64\,S^3.$$

Evidently then, by precisely the same process, the discriminant of the surface

$$ax^3+by^3+cz^3+du^3+ev^3$$

is the result of clearing of radicals the equation

$$\sqrt{bcde}+\sqrt{cdea}+\sqrt{deab}+\sqrt{eabc}+\sqrt{abcd}=0;$$

and on performing the operation the result is found to be

$$\{A^2-64B\}^2=16384\{D+2AC\};$$

where A, B, C, D are the fundamental invariants described above.

It is evident, in like manner, that if it be required to find the result of elimination between three ternary quadrics, since we can write these functions in the form

$$\begin{aligned} &a\,x^2+by^2+cz^2+du^2, \\ &a'x^2+b'y^2+c'z^2+d'u^2, \\ &a''x^2+b''y^2+c''z^2+d''u^2, \end{aligned}$$

we can reduce these to the form

$$\alpha x^2=\beta y^2=\gamma z^2=\delta u^2;$$

that therefore, as before, the eliminant can be expressed as the result of clearing of radicals an equation of the form

$$\sqrt{\beta\gamma\delta}+\sqrt{\gamma\delta\alpha}+\sqrt{\alpha\beta\delta}+\sqrt{\alpha\beta\gamma}=0,$$

and therefore, as Mr. SYLVESTER first pointed out, the eliminant is of the form

$$T^2=64\,S.$$

But in this case S is not a perfect cube, as it turns out in the problem of finding the

discriminant of a cubic. In fact, in this case S is the product of the four determinants of the system

$$\begin{Vmatrix} a, & b, & c, & d \\ a', & b', & c', & d' \\ a'', & b'', & c'', & d'' \end{Vmatrix}$$

and therefore its vanishing expresses the condition that some one of the quadrics of the system $\lambda U+\mu U'+\nu U''$ shall be a perfect square; or geometrically, it expresses the condition that it shall be possible, through the intersection of two conics of the system, to draw a conic having double contact with the third. In this case the Jacobian of the system breaks up into a right line and conic.

But we cannot, in like manner, conclude that the result of elimination between four quaternary quadrics is expressible as the result of clearing of radicals the sum of five square roots, because the quadrics cannot in general be expressed as four functions each of the form

$$ax^3+by^3+cz^3+du^3+ev^3.$$

We proceed now, from the consideration of the invariants of a quaternary cubic, to that of its covariants. To the number of these, however, there is, as far as I am aware, no limit, and I must therefore confine myself to enumerating some of the simplest and most important. Of covariants of the first order in the variables, the following may be regarded as the four fundamental forms. The simplest, L, of the eleventh order in the coefficients,

$$L=a^3b^3c^3d^3e^3\{ax+by+cz+du+ev\};$$

of the nineteenth order in the coefficients,

$$L'=a^5b^5c^5d^5e^5\{bcdex+cdeay+deabz+eabcu+abcdv\};$$

of the twenty-seventh order,

$$L''=a^9b^9c^9d^9e^9\{a^3x+b^3y+c^3z+d^3u+e^3v\}.$$

There is no covariant of the first order in the variables and 35th in the coefficients which may not be expressed in terms of the preceding three and the fundamental invariants; but we have a fourth of the 43rd order, viz.

$$L'''=a^{13}b^{13}c^{13}d^{13}e^{13}\{a^3x+b^3y+c^3z+d^3u+e^3v\}.$$

Every other covariant can be expressed in terms of these four. The resultant of these four covariants, that is to say, the condition that they shall represent four planes meeting in a point, is the invariant F of the 100th degree already noticed. The cubic itself can be expressed as a function of L, L', L'', L''' having invariant coefficients, which expression M. Hermite calls the form-type of the function. I have not thought it worth while to undertake the labour of finding the actual values of the coefficients of the function so transformed.

The simplest linear contravariant is of the 13th degree, that of the 5th vanishing, as

before mentioned. It is

$$abcde\Sigma(a-b)(\alpha-\beta)\{(a+b)c^3d^3e^3-abcde(cd+de+ec)\}.$$

The coefficient of α in this is

$$abcde\{A-5b^3c^3d^3e^3+5abcde(bcd+bce+bcd+cde)\},$$

A being the simplest invariant.

The next linear contravariant is of the 21st degree,

$$a^4b^4c^4d^4e^4\Sigma(a-b)(\alpha-\beta).$$

The next is of the 29th degree,

$$a^3b^3c^3d^3e^3\Sigma cde(a-b)(\alpha-\beta),$$

and so on.

The simplest covariant quadric is of the 6th degree,

$$abcde(ax^2+by^2+cz^2+du^2+ev^2).$$

The next of the 14th degree,

$$a^3b^3c^3d^3e^3\Sigma ab(cd+de+ec)xy,$$

which may also be written

$$a^3b^3c^3d^3e^3\Sigma(bcde-abcd-abce-abde-acde)x^2.$$

The next of the 22nd degree, may most simply be written

$$a^4b^4c^4d^4e^4(a^2x^2+b^2y^2+c^2z^2+d^2u^2+e^2v^2).$$

That of the 30th is

$$a^5b^5c^5d^5e^5(x^2+y^2+z^2+u^2+v^2),$$

and so on.

The contravariant quadrics are—

10th order; $a^2b^2c^2d^2e^2\Sigma(\alpha-\beta)^2$.

18th order; $a^3b^3c^3d^3e^3\Sigma cde(\alpha-\beta)^2$, &c.

The covariant cubics are—

9th order; $\Sigma cde(a+b)abcde\,zuv$

17th order; $a^3b^3c^3d^3e^3(a^2x^2+b^2y^2+c^2z^2+d^2u^2+e^2v^2)$.

This last covariant is important, because we can immediately deduce from it, that the operation

$$t^3\left(a^2\frac{d}{da}+b^2\frac{d}{db}+c^2\frac{d}{dc}+d^2\frac{d}{dd}+e^2\frac{d}{de}\right)$$

performed on any invariant or covariant of the cubic

$$ax^3+by^3+cz^3+du^3+ev^3$$

gives rise to a new invariant or covariant of the cubic, and of the degree sixteen higher in the coefficients. It is on this account that I think it enough to write down two covariants of each degree in the variables.

The simplest contravariant of the third order is the evectant of the invariant A, which is of the seventh order in the coefficients. It is

$$\Sigma c^3d^3e^3(a-b)(\alpha-\beta)^3-\Sigma abcd^3e^3(2\alpha-\beta-\gamma)(2\beta-\gamma-\alpha)(2\gamma-\alpha-\beta).$$

The next is of the fifteenth,

$$\Sigma a^3b^3c^3d^3e^3(bcde)(a-b)(\alpha-\gamma)(\alpha-\delta)(\alpha-\varepsilon).$$

After the Hessian, the simplest covariant quartic is

$$a^3b^3c^3d^3e^3(a^3x^4+b^3y^4+c^3z^4+d^3u^4+e^3v^4).$$

We have already mentioned the simplest contravariant quartic, viz.

$$S=\Sigma bcde(\alpha-\beta)(\alpha-\gamma)(\alpha-\delta)(\alpha-\varepsilon).$$

The reciprocant of the cubic is $64S^3=T^2$, where T is the contravariant sextic,

$$\begin{aligned}T=&\Sigma c^3d^3e^3(\alpha-\beta)^6-2\Sigma bcd^3e^3(\alpha-\beta)^3(\alpha-\gamma)^3\\&+2\Sigma abcde^3\{(\alpha-\gamma)(\beta-\delta)-(\alpha-\delta)(\gamma-\beta)\}\{(\alpha-\delta)(\gamma-\beta)-(\alpha-\beta)(\delta-\gamma)\}\\&\{(\alpha-\beta)(\delta-\gamma)-(\alpha-\gamma)(\beta-\delta)\}.\end{aligned}$$

I have already mentioned the covariant quintic

$$\Phi=abcde\Sigma(abx^2y^2z),$$

which, however, may be replaced by

$$abcde(a^3x^5+b^3y^5+c^3z^5+d^3u^5+e^3v^5),$$

the two differing only by the product of the original cubic and the simplest covariant quadric.

The simplest covariant of the fifteenth order in the coefficients and fifth in the variables, is what may be called the canonizant $a^3b^3c^3d^3e^3xyzuv$, since it represents the five planes of the canonical form.

The only covariant of higher order which we shall notice is that of the ninth order, which we shall call the covariant Θ, viz. the determinant,

$$\begin{vmatrix}\frac{d^2U}{dx^2}, & \frac{d^2U}{dxdy}, & \frac{d^2U}{dxdz}, & \frac{d^2U}{dxd\omega}, & \frac{dH}{dx}\\ \frac{d^2U}{dydx}, & \frac{d^2U}{dy^2}, & \frac{d^2U}{dydz}, & \frac{d^2U}{dyd\omega}, & \frac{dH}{dy}\\ \frac{d^2U}{dzdx}, & \frac{d^2U}{dzdy}, & \frac{d^2U}{dz^2}, & \frac{d^2U}{dzd\omega}, & \frac{dH}{dz}\\ \frac{d^2U}{d\omega dx}, & \frac{d^2U}{d\omega dy}, & \frac{d^2U}{d\omega dy}, & \frac{d^2U}{d\omega^2}, & \frac{dH}{d\omega}\\ \frac{dH}{dx}, & \frac{dH}{dy}, & \frac{dH}{dz}, & \frac{dH}{d\omega}. & \end{vmatrix}$$

The importance of this covariant consists in this, that the twenty-seven right lines on the cubic are determined as the intersection with the given cubic of the surface of the ninth order, $\Theta=4H\Phi$, where Φ is the covariant of the fifth order just mentioned. This can be verified with little labour by taking the general equation of a surface passing

through the line xy and examining the terms in Θ, H, and Φ, which do not contain x or y. I have already noticed* that the existence of these twenty-seven right lines may be deduced as a particular case of the following theorem, that on a surface of the nth degree there is a locus of points at each of which it is possible to draw a line to meet the surface in four consecutive points, this locus being the intersection of the given surface with a surface of the degree $11n-24$. I gave the equation of this surface, but in a very inconvenient form†. But I have now to add a simpler form of the general equation of this surface, viz.

$$\Theta = 4\mathrm{H}(\Phi + a\Psi),$$

where Θ, H, Φ have the meaning already explained; a is a numerical multiplier $\left(\frac{(n-2)(n-3)}{1.2}\right)$, and Ψ is a covariant obtained as follows:—Let Θ when expanded be

$$\mathrm{A}\left(\frac{d\mathrm{H}}{dx}\right)^2 + \mathrm{B}\left(\frac{d\mathrm{H}}{dy}\right)^2 + \&c. + 2\mathrm{A}'\frac{d\mathrm{H}}{dx}\frac{d\mathrm{H}}{dy} + \&c.,$$

then

$$\Psi = \left\{\mathrm{A}\frac{d^2}{dx^2} + \mathrm{B}\frac{d^2}{dy^2} + \&c. + 2\mathrm{A}'\frac{d^2}{dxdy} + \&c.\right\}^3 \mathrm{U};$$

that is to say, Ψ is the result of squaring the bordered Hessian, introducing differential symbols instead of the contravariant variables, and operating with the result on U. In the case of the cubic Ψ evidently vanishes.

* Cambridge and Dublin Mathematical Journal, vol. iv. p. 258.

† Quarterly Journal of Mathematics, vol. i. p. 336.

XV. *On Isoprene and Caoutchine.* By C. Greville Williams.

Received June 4,—Read June 21, 1860.

The products of the destructive distillation of caoutchouc have been studied by several chemists. The results at present obtained are, however, quite irreconcileable. Gregory* appears to have been the first to direct attention to them, but it is evident that even at the time of writing his 'Handbook of Organic Chemistry' he was far from considering the true nature of the products as having been ascertained; for, at p. 346, he says, "When exposed to heat, caoutchouc first melts, and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbo-hydrogens. Some of these oils boil at 90°, others at 680° Fahr.; and at intermediate points I found that one highly rectified oil which boiled at 96°, and had the composition of olefiant gas, when acted on by sulphuric acid, yielded an oil which boiled at 428°, and had the same composition. But most of these oils have the composition of oil of turpentine, C^5H^4, or $C^{10}H^8$. One of them, called *caoutchine*, gives with chlorine an oil, $C^{10}H^8+Cl$." Now the above statement contains undoubtedly the best account that could be given in so short a space, of the results that had been obtained up to the time of publication of the work alluded to, but the account is somewhat confused, because the various observers all differ immensely in their results. The expressions C^5H^4 and $C^{10}H^8$, as used by Gregory, merely indicate arithmetical relations, and were not to be received as definite formulæ; for, in the first place, C^5H^4 is, according to our present views, an impossible formula†, and in the next, caoutchine is $C^{30}H^{16}$, not $C^{10}H^8$. No chemist up to the present time has proved a hydrocarbon of the formula $C^{10}H^8$ (=4 volumes of vapour) to exist among the products of the distillation of caoutchouc. Such a formula, if proved, would be interesting, because turpentine being the starting-point for Kopp's empirical formula for boiling-points, any substance having exactly half the number of atoms of carbon and hydrogen, with the same vapour-volume, would serve as the point of departure of numerous speculations upon boiling-points generally. The results of M. Bouchardat‡ are curious, and not easy to understand. He obtains olefiants and eupione, but no bodies of the formula $n(C^5H^4)$, while Himly§ obtains bodies of the latter formula and no olefiants. The annexed Table contains the results of the three chemists alluded to.

* Ann. der Chem. und Pharm. vol. xvi. p. 61.

† C=6, H=1, O=8.

‡ Ann. der Chem. und Pharm. vol. xxvii. p. 30.

§ Ibid. p. 40.

Name of observer.	Fluid found.	Boiling-point.	Density.	
			Liquid.	Vapour.
Gregory	$C^n H^n$	36°	0·654	
Bouchardat	$C^5 H^8$	below 0	0·630 at 4°	
Bouchardat	Caoutchène ($C^{10} H^8$)	14·5	0·650	
Bouchardat	Eupione (?)	51	0·690 at 15°	
Himly	$C^5 H^4$ (?)	30—40		
Himly	Caoutchine ($C^{20} H^{16}$)	171	0·842	4·461
Bouchardat	Hévéène ($C^n H^n$)	above 315	0·921 at 21°	

Results so contradictory would almost lead one to suppose that, like castor oil, caoutchouc yielded different products according to the temperature, but in that case the distillate obtained in a carefully conducted experiment should contain bodies belonging to the olefiants and the terebenes; this, however, is not the case. The weight of evidence appearing to prove olefiants to be the principal products, I had some hopes that caoutchouc, if carefully distilled, would yield hydrocarbons from which I might obtain certain at present unknown hydriodic ethers and their derivatives, in accordance with reactions first imagined by M. Berthelot, thus:—

$$\underbrace{C^n H^n + H I}_{\text{Olefiant plus hydriodic acid.}} = \underbrace{(C^n H^{n+1}) + I}_{\text{Iodide of alcohol radical.}}$$

But I soon found that caoutchouc, when carefully distilled in iron vessels, yielded no olefiant whatever. This is, moreover, in perfect accordance with experiments made by me some years ago*, in which I showed that caoutchouc, like many other oils, decolorized the same quantity of bromine as oil of turpentine. A repetition of this experiment, made with great precaution to ensure success, will be found further on.

The distillation was conducted with care in an iron alembic, the lowest temperature being used consistent with the distillation of oils. In fact I even stopped the distillation before the whole of the last oil, hévéène, came over, in order to ensure the decomposition taking place in the simplest manner. The crude distillate was very fœtid, and contained traces of volatile bases derived from the decomposition of a minute trace of vegetable caseine in the caoutchouc. The bases were removed by agitation of the oil with dilute sulphuric acid; the latter was then got rid of by washing with water, which, in its turn, was subsequently removed by digestion with sticks of potash. The fluid thus prepared was easily separated by fractional distillation into two portions, one boiling between 37° and 44° C., and the other between 170° and 180°. The fractional separation of the hydrocarbons in the crude distillate affords a very instructive example of the extraordinary extent to which boiling-points are lowered by successive rectifications. In the first rectification the product was very small, below 116° C. The greater part

* "On a Process for estimating the Equivalents of some Fluid Hydrocarbons by means of Bromine," Chemical Gazette, 1853.

distilled between 116° and 198°. Only one-half came over below 204°. In the second rectification a large fraction was obtained between 40° and 50°, then scarcely any distilled until between 170° and 180°, which latter fraction was very large. At 171° the thermometer was often perfectly steady while an ounce distilled over, the entire contents of the retort not being much more than one and a half ounce. The lower fraction oscillated between 36° and 44°, the variability in its boiling-point being principally due to the presence of oxygen; for, by careful and repeated rectifications over sodium, it may be made to distil almost entirely between 37° and 38°. This fluid lies at the boundary line between gases and liquids: it is scarcely possible to wet the hand with it; and if poured from a moderate height in small drops, it is volatilized before reaching the floor. A very pretty way of observing the influence of small pressures upon its physical condition, consists in passing a few drops into a mercurial eudiometer standing vertically. The warmth of the hand applied to the top of the instrument is sufficient to convert it into vapour; but if the position of the eudiometer be then altered so as to stand almost horizontally, the increase of pressure is sufficient to condense the gas into a liquid, and, on the other hand, it is instantly vaporized again on restoring the eudiometer to its original position.

This hydrocarbon possesses a property which, even more than its extreme volatility, renders it troublesome to the analyst. Unlike very volatile fluids in general, it lines with a slight film of carbon the bulbs in which it is contained during combustion. It is true that the amount thus left is very small, but it is sufficient to render an exact determination of the carbon difficult. It being of course necessary to have all the apparatus, oxide of copper, &c. as cold as possible, it was also not easy to keep the hydrogen as low as could be desired. The substance used in the first three analyses boiled between 37° and 38°, and was prepared from gutta percha. No. IV. boiled between 42° and 43°, and No. V. between 43° and 44°.

I. 0·1848 grm. yielded 0·5985 carbonic acid and 0·1998 water.
II. 0·1770 grm. yielded 0·5696 carbonic acid and 0·1963 water.
III. 0·2076 grm. yielded 0·6689 carbonic acid and 0·2264 water.
IV. 0·1730 grm. yielded 0·5570 carbonic acid and 0·1898 water.
V. 0·1362 grm. yielded 0·4398 carbonic acid and 0·1504 water.

Or, in per-centages:—

	Experiment.					Mean.	Calculation.		
	I.	II.	III.	IV.	V.				
Carbon . .	88·3	87·8	87·9	87·8	88·1	88·0	C^{10}	60	88·2
Hydrogen .	12·0	12·0	12·1	12·2	12·3	12·1	H^{8}	8	11·8
								68	100·0

leading to the empirical relation

$$\frac{n\,(C^{5}H^{4})}{2 \times 2}.$$

Although the boiling-point indicated the value of n to be not greater than 2, it is plain that the fluid might possibly have a higher formula. The atomic weight was therefore determined from the density of the vapour, assuming it to possess the usual condensation to four volumes.

The following were the numbers obtained:—

Weight of fluid.	Temperature of vapour.	Difference of level, in millims.	Pressing column of water reduced to millimetres of mercury.	Atmospheric pressure, in millimetres.	Observed volume, in cubic centimetres.	Density of vapour.
0·0882	43°	126	25	764	36·7	2·47
0·0848	58	124	25	765	37·8	2·40
0·0882	61	119	24	764	38·6	2·46
0·0964	64	99·1	31	764·4	41·0	2·45
0·0882	68	113	24	764	39·4	2·43

The formula $C^{10}H^8$ requires

10 volumes Carbon-vapour . . . . 0·8290 . 10 = 8·2900

16 volumes Hydrogen . . . . . 0·0692 . 16 = 1·1072

$$\frac{9\cdot3972}{4} = 2\cdot3493$$

Mean of experiments.	Theory, $C^{10}H^8$ = 4 volumes.
2·44	2·3493

The values condensed into the above Table are not intended to represent the influence of temperature upon the density. They are cited to show unmistakeably the formula of the hydrocarbon. It will be seen at a glance that all the determinations except the second are higher than is consistent with perfect accuracy. This is dependent upon the extreme tendency of the fluid to undergo oxidation, and thus, to a greater or less extent, lose its volatility. It was some time before the full extent of this tendency was ascertained and precautions taken to prevent it, and in the meantime the densities came out too high. It was found, however, that if distilled over sodium only a few minutes before determining the volume of the vapour, the result obtained was sufficiently accurate for the purpose required. The second of the experiments in the above Table was made with this precaution, and the resulting number was only 0·05 in excess of the calculation.

I have given the substance thus examined the name of *isoprene*. It would have been more grateful to me to have retained one of the names given by the previous observers, if that course had been possible; but Himly has not named the fluid discovered by him boiling between 33° and 44°, and the term *caoutchène* having been applied by Bouchardat to a fluid boiling at 14°·5, I could not adopt it; moreover, it is too like *caoutchine*.

The specific gravity of the fluid at 20° C. was found to be 0·6823.

It will be seen that none of the hydrocarbons examined by Gregory, Himly, or

Bouchardat can be identified with that just described; and although the formulæ $C^5 H^4$ and $C^{10} H^8$ have often been vaguely applied to the numerous isomers of turpentine, yet none of the hydrocarbons obtained by the above chemists have been shown to contain $C^{10} H^8$ *for four volumes of vapour*. The hydrocarbon discovered by Couerbe* in the fluid obtained by the powerful compression of resin gas, although of the same composition, differs too much in density (0·709) and boiling-point (50°) to be considered as identical.

Action of Atmospheric Oxygen on Isoprene.

If isoprene be left in a partly filled bottle for some months, it gradually loses its fluidity, and at last even becomes quite viscid; at the same time it is found to have acquired powerful bleaching properties. It readily decolorizes sulphate of indigo, and, under certain circumstances, converts sulphide of lead into sulphate. It is, in fact, ozonized.

Schönbein was the first to show that oil of turpentine absorbed ozone when kept for a long time, and I subsequently observed several cases where ozone was capable of existing in contact with organic and inorganic matters without exerting any material action on them so long as the temperature was kept down. In these instances, immediately the heat rose beyond a certain point, the substance in contact with the ozone underwent oxidation. Thus, if a slip of lead test-paper be exposed to the vapours of sulphide of hydrogen until the paper has acquired a deep brown colour, and a drop of an ozonized oil be placed on it, no change ensues at ordinary temperatures; but if the paper moistened with the oil be warmed until the latter begins to volatilize, the sulphide is immediately oxidized and bleached.

But the most remarkable phenomenon perhaps yet known in connexion with the ozonization of essential oils, takes place on submitting ozonized isoprene to distillation. If the temperature be kept as low as is compatible with the volatilization of the unaltered portion of the oil, a colourless limpid fluid distils over, having the composition and boiling-point of pure isoprene. As the operation proceeds the fluid thickens, causing the temperature to rise somewhat suddenly. The ozone at this point instantly begins to act with energy, a cloudy vapour rises, accompanied by an intensely sharp odour, and the contents of the retort instantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers. When pure, it is opake; but if allowed to become exposed to the air, especially when warm, it becomes transparent, first on the edges, and subsequently throughout the whole mass. When burnt, it exhales the peculiar odour hitherto considered characteristic of caoutchouc itself. It is not easy to prepare or to preserve this substance of definite composition. If the heat be allowed to rise too rapidly during its formation, it becomes decomposed; and if not heated sufficiently, a portion of the original hydrocarbon obstinately adheres, in spite of its extreme volatility when separate. However prepared, its

* Ann. de Chim. et de Phys. vol. lxix. p. 184. Journ. Prakt. Chem. vol. xviii. p. 165. Gmelin's Handbook, vol. x. p. 411. Cav. Soc. Transl.

composition is that of isoprene plus oxygen. If sufficient care be taken, the oxidation is perfectly definite. A specimen prepared with every precaution, and immediately analysed, afforded, on combustion with oxide of copper and oxygen gas, the annexed numbers:—

0·1796 grm. gave 0·5186 carbonic acid and 0·1732 water.

Converting these values into per-centages, we have—

	Experiment.	Calculation.		
Carbon . . .	78·8	C^{10}	60	78·95
Hydrogen . .	10·7	H_8	8	10·52
Oxygen . . .	10·5	O	8	10·53
	100·0		76	100·00

The above values at once indicate

$$C^{10}H^{8}O$$

as the formula for the substance; the agreement of the numbers resulting from the analysis with those of calculation appearing to show conclusively the perfectly definite nature of the reaction.

As regards the true formula of this substance, there is reason to suppose that the expression $C^{10}H^{8}O$ does not correspond to four volumes of vapour; but as it is not volatile without decomposition, and as its properties forbid any hope of its yielding compounds from which the true equivalent might be deduced, I am at present compelled to rest satisfied with obtaining the simplest arithmetical relation between the elements.

The above-described substance is, it is believed, unique in its characters, whether we regard its composition as the directly formed oxide of a hydrocarbon, or the mode of its production by the influence of ozone.

On Caoutchine.

The formula derived by M. Himly from his experiments upon the oil boiling between 171° and 173° was perfectly correct. The following numbers resulting from my analyses merely, therefore, confirm the old ones.

Nos. II. and III. were made on two samples of caoutchine from gutta percha. No. II. boiled between 170° and 173°, and No. III. between 173° and 177°. Owing to the large quantity of carbon deposited in the bulbs, I was obliged to burn the fluid in open tubes, and use oxygen in excess at the termination of each analysis.

I. 0·1808 grm. yielded 0·5828 carbonic acid and 0·1932 water.
II. 0·1992 grm. yielded 0·6462 carbonic acid and 0·2214 water.
III. 0·1974 grm. yielded 0·6362 carbonic acid and 0·2098 water.

The above numbers, converted into per-centages, yield the following values, which are placed parallel with the theoretical formula and the previous results of M. Himly:—

	Experiment.					Calculation.		
	I.	II.	III.	Mean.	Himly.			
Carbon . .	87·9	88·5	87·9	88·1	88·44	C^{20}	120	88·2
Hydrogen .	11·9	12·1	11·8	11·9	11·56	H^{16}	16	11·8
							136	100·0

I re-determined the vapour-density by Gay-Lussac's process with the following result:—

Temperature of vapour	192°
Weight of substance	0·1530 gramme.
Difference of level	52·0 millimetres.
Oil column reduced to millimetres of mercury . .	22·0 millimetres.
Atmospheric pressure	747·0 millimetres.
Observed volume	46·0 cubic centimetres.
Density	4·647

The formula $C^{20}H^{16}$ requires—

20 volumes of Carbon-vapour . . .	0·8290 . 20 = 16·5800
32 volumes of Hydrogen	0·0692 . 32 = 2·2144
	$\frac{18·7944}{4} = 4·6986$

Experiment.	Himly.	Calculation = 4 volumes.
4·647	4·461	4·6986

In consequence of the high temperature at which the experiment was made, it became necessary to introduce into the formula a correction for the elastic force of the vapour of mercury.

On the Relation between the first and second Hydrocarbons produced by distillation of Caoutchouc.

We are now, for the first time, in a position to understand the true connexion between the two hydrocarbons which have been described. The relation between them is the same as that between amylene and paramylene, and, as in the case of those bodies, the second is twice as heavy in the state of vapour as the first.

The boiling-points of these bodies show very strongly the limited power of empirical formulæ, even when (like those of Kopp and Gerhardt) founded on the accurate observation of a vast number of bodies. Thus, amylene, $C^{20}H^{20}$, containing four atoms of hydrogen more than caoutchine, should boil, according to Gerhardt's law, $15 \times 2 = 30°$ lower than that body, whereas the boiling-point is only 11° lower. Again, amylene, containing two atoms of hydrogen more than isoprene, should boil 15° lower, whereas it boils 2° higher.

The reduplication of a formula has not the same *relative* influence upon the boiling-point of amylene that it has upon that of isoprene; thus—

Paramylene, $C^{30}H^{30}$, boils at	160°	Caoutchine, $C^{30}H^{16}$, boils at	171°
Amylene, $C^{10}H^{10}$, boils at	39°	Isoprene, $C^{10}H^{8}$, boils at	37°
Difference . . .	121	Difference . . .	134

Oil of turpentine boils at 160°, and is taken as the pivot round which the boiling-points of hydrocarbons should arrange themselves at distances proportioned to the number of atoms of carbon and hydrogen in their formulæ; yet caoutchine, which not only has the same formula, but gives almost identical reactions, boils at 171°, eleven degrees higher, and very near that of carvene, which is 173°.

Comparative experiments on the Action of Bromine on Caoutchine and Oil of Turpentine.

M. Himly had observed that chlorine and bromine act upon caoutchine, and that the products when distilled over a base afforded an oil containing less hydrogen than caoutchine. He did not examine the nature of the reaction more closely.

I mentioned at the commencement of this paper that I had several years ago made an experiment on the mutual action of bromine and caoutchine, which led me to believe the latter to belong, not to the olefiant, but to the vast group of hydrocarbons isomeric with oil of turpentine. But that experiment having been made with the bromine and hydrocarbon undiluted, and, moreover, the caoutchine not having been prepared by myself, I considered it necessary to repeat it with several precautions not then observed.

The action of bromine upon the terebenes is peculiar, one atom, or four-volume equivalent, always requiring exactly four atoms of bromine to produce a colourless fluid. If the hydrocarbon and the bromine be diluted, the former with alcohol, the latter with water, the experiment may be made with considerable precision. For the purpose of comparing the isomers, I prepared some freshly dried and rectified turpentine and caoutchine. They were diluted with sufficient alcohol for each of the resulting fluids to contain exactly ten per cent. of hydrocarbon. The bromine employed was in the state of a weak solution in water, twenty cubic centimetres containing 0·2527 of bromine. A small flask containing twenty cubic centimetres with the stopper in its place, was employed each time to measure the bromine water, which was transferred to a large stoppered flask, every precaution being taken to prevent loss. The diluted hydrocarbon was then gradually dropped into the bromine water from a Schüster's alkalimeter containing a weighed quantity. Considerable agitation was applied after each addition. When the bromine water was nearly decolorized, the liquid was added very cautiously, and an interval of about half a minute allowed to elapse between each addition. When the fluid had become perfectly colourless, the alkalimeter was reweighed. The following numbers were obtained in eight experiments made in the manner described:—

Quantity of Bromine water used in each experiment 20 cub. cents.

Turpentine experiments.			Caoutchine experiments.		
Number.	Difference in weight of the alkalimeter before and after the experiment.	Oil of turpentine required to decolorise 20 cub. cents. of bromine water.	Number.	Difference in weight of the alkalimeter before and after experiment.	Caoutchine required to decolorise 20 cub. cents. of bromine water.
	grm.	grm.		grm.	grm.
I.	1·070	0·1070	I.	1·119	0·1119
II.	1·137	0·1137	II.	1·088	0·1088
III.	1·066	0·1066	III.	1·083	0·1083
IV.	1·024	0·1024	IV.	1·074	0·1074

Mean of turpentine experiments. 0·1074

Mean of caoutchine experiments. 0·1091

The identity of behaviour of caoutchine and oil of turpentine becomes very evident from the above experiments. The mean of the caoutchine results is nevertheless somewhat higher than that of the turpentine series; I ascribe this to caoutchine being, to a very slight degree, more sluggish in its action than oil of turpentine.

On the Action of Bromine on Isoprene.

I was exceedingly desirous of making experiments with weighed quantities of isoprene and bromine, in order to compare it with caoutchine. With this intent I made a solution of it in alcohol, the strength being the same as the turpentine and caoutchine solutions. But it was impossible to obtain the wished-for results, owing to the manner in which the isoprene volatilized from the solution while pouring it into the bromine water.

Isoprene combines explosively with bromine, even in presence of seventy or eighty times its volume of water. When the vessel containing the bromine at the bottom and the isoprene on the surface is shaken, union takes place with a loud noise and considerable evolution of heat. A fine mobile bromine compound is the result. When cohobated with excess of hydrate of potash, the greater portion is entirely decomposed, yielding a black mass, the distillate having the same odour as that evolved under similar circumstances by the higher olefiant, but accompanied by a substance so irritating to the eyes as to render it very distressing to manipulate. On placing about one ounce in a flask, and adding a fragment of hydrate of potash to neutralize it, an explosion took place, the fluid being thrown in my face and causing the most intense pain in the eyes. For several days no person could enter the laboratory without incurring great pain, accompanied by profuse lacrymation. My substance having in this unfortunate manner been lost, I am compelled to defer a more minute investigation of it.

On the Conversion of Caoutchine into Cymole and Paracymole.

In Gerhardt's classification of organic bodies, oil of turpentine is made to belong to the cymenic series; and it is even stated that Deville, by passing turpentine and carbonic acid through a tube heated to dull redness, obtained an oil which appeared to contain

$C^{20}H^{16}$; carbonic oxide, water, and empyreumatic products being formed simultaneously. Disregarding the empyreumatic bodies, the following equation may be considered to explain the nature of the reaction:—

$$\underbrace{C^{20}H^{16}}_{\text{4 vols. oil of turpentine.}} + \underbrace{C^{2}O^{4}}_{\text{4 vols. carbonic acid.}} = \underbrace{C^{20}H^{14}}_{\text{4 vols. cymole.}} + \underbrace{2HO}_{\text{4 vols. water.}} + \underbrace{2CO}_{\text{4 vols. carbonic oxide.}}$$

Some experiments made by me a considerable time ago with oil of turpentine, led me to conceive the idea of converting it into cymole, or an isomer, by the alternate action of bromine and a highly electro-positive metal, and the identity in certain cases of the reactions of oil of turpentine and caoutchine rendered it probable that a similar product would be yielded with the latter. Experiment has completely confirmed this supposition.

If to a quantity of bromine and water in a stoppered flask caoutchine be gradually added, and the flask be shaken after each addition, a sharp hissing sound is heard, and combination takes place with great energy and considerable rise of temperature; at the same time a heavy oil, red at first but finally colourless, sinks to the bottom. The product when cold is as viscid as treacle. Its characters do not offer any great guarantee for purity; and the production of hydrobromic acid at the same time, indicates that while one portion of the halogen combines with the caoutchine, another seizes the most easily removeable of its atoms of hydrogen, and yields the acid which is found dissolved in the water.

I examined the reaction which takes place with turpentine under these circumstances some years ago, but at that time I was not fully alive to the true explanation, because I had not treated the resulting oil with alcoholic potash or sodium. The analyses I then made indicated the formula of the oil from turpentine to be $C^{20}H^{15}Br, 2Br, 2HO$. One equivalent of hydrobromic acid was always found in the watery fluid. Assuming this to be correct, as I have no doubt it is, we have

$$C^{20}H^{16} + 4Br + 2HO = C^{20}H^{15}Br, 2Br, 2HO + HBr.$$

Every four equivalents of bromine yield, therefore, one equivalent of hydrobromic acid; and in an experiment where 33·2 parts of bromine were employed, 8·2 of hydrobromic acid were found in the aqueous fluid. If the above equation be correct, 8·4 should have been obtained.

The oil produced as above from caoutchine, when heated, yields torrents of hydrobromic acid, and an oil distils over containing less bromine and hydrogen. When cohobated with sodium in excess, a very fragrant and perfectly colourless hydrocarbon was produced, distilling between 171° and 200°. It was received in four portions: *a*, between 171° and 177°; *b*, 177° to 181°; *c*, 181° to 186°; and *d*, 186° to 200°. A yellowish oil remained behind at this point; it required a very much higher temperature for distillation, and on cooling deposited a few very minute crystals.

Caoutchine and turpentine behave in a precisely similar manner with the above

reagents; and it is worthy of observation that the resulting hydrocarbon has the same peculiar odour, from whichever source it is prepared *.

In the following analyses, I. was made on a product from turpentine, II. was fraction *b*, and III. was fraction *d*. Fraction *a* was rejected, as it appeared to contain traces of the original hydrocarbon, regenerated in the same manner I have shown to take place with brominized heptylene and octylene.

I. 0·1550 grm. gave 0·5070 carbonic acid and 0·1466 water.
II. 0·1918 grm. gave 0·6292 carbonic acid and 0·1790 water.
III. 0·2100 grm. gave 0·6892 carbonic acid and 0·1968 water.

Or, per cent.,—

	Experiment.			Mean.	Calculation.		
Carbon .	89·2	89·5	89·5	89·4	C^{20}	120	89·6
Hydrogen	10·5	10·4	10·4	10·4	H^{14}	14	10·4
						134	100·0

The above numbers completely correspond with the formula

$$C^{20}H^{14},$$

which is evidently that of cymole. Moreover the density of the fluid, 0·8664 at 20°, was almost the same as that given by GERHARDT, namely, 0·8610 at 14°.

I could have wished to give equations expressive of the entire decompositions which take place, and it would be easy to do so were I to disregard, or consider as merely accidental, the substances formed at the same time. When the brominized oil is distilled, before or after treatment with alcoholic potash, nearly fifty per cent. of loss is incurred. The retort contains a black carbonaceous mass, occupying two-thirds of its capacity. A similar phenomenon occurs in the treatment with sodium; and at the same time, as I have said, a certain portion of caoutchine or turpentine, as the case may be, is regenerated.

The yellow oil of high boiling-point previously alluded to, exists in very small quantity among the products formed by the action of sodium on brominized caoutchine; probably not more than one-tenth of the distillate boils above 200° C., whereas the yellow oil boils only a little below 300° C. The quantity in my possession was far too small to allow of a determination of this point. In composition, however, it agreed with that of cymole.

0·2224 grm. gave 0·7312 carbonic acid and 0·2022 water.

	Experiment.	Calculation.		
Carbon . .	89·7	C^{20}	120	89·6
Hydrogen .	10·1	H^{14}	14	10·4
			134	100·0

* Since writing the above, I have compared the cymole from caoutchine, and that from oil of turpentine, with a specimen of the same hydrocarbon, prepared with great care from oil of cumin by my friend Mr. CHURCH; the odour in each case was absolutely identical.

The crystalline substance was in exceedingly minute quantity. It is far from impossible that it may be the radical thymyle formed from its hydruret cymole by the action of the bromine. As it would have the composition $C^{20}H^{25}=2C^{10}H^{13}$, the probability is that it would be a crystalline solid. This also would account for the low hydrogen and the high carbon.

The exceedingly high boiling-point of the yellow oil is such strong evidence of its being a polymeric condition of cymole, that I have provisionally named it *paracymole*.

Conversion of the Cymole from Turpentine and Caoutchine into Insolinic Acid.

Although the experiments detailed left little doubt upon my mind of the identity of the cymole from turpentine and caoutchine with that from cumin oil, still the number of isomeric bodies continually being discovered is so great, that it is highly desirable to make a crucial experiment whenever possible. The exceedingly characteristic properties of insolinic acid rendered it peculiarly suitable in the present instance. Dr. HOFMANN has shown it to be a product of the oxidation of cuminic acid and cymole under the influence of chromic acid. The quantity of cymole in my possession was so small (about two drachms), that there would have been little hope of success had the reaction been less definite. On cohobating it with eight parts of sulphuric acid, eight of bichromate of potash, and twelve of water, for a few minutes, white flocks became apparent; they continually increased until their bulk equalled that of the cymole employed. The crude acid was dissolved in ammonia and, after filtration, precipitated by hydrochloric acid. It was washed, first with warm water, then with boiling alcohol, and, finally, with ether. Thus purified it was quite colourless. It was then dissolved in ammonia, and the solution evaporated until crystals of the acid salt began to form. The solution, rendered faintly alkaline by the cautious addition of ammonia, was precipitated by nitrate of silver, care being taken to keep it slightly alkaline to prevent the separation of any insolinic acid. The salt, after drying at 100° until it ceased to lose weight, was ignited, during which operation it evolved the peculiar aromatic odour so characteristic of all the insolinates when heated strongly. In this manner I prepared three specimens,—*a*, from turpentine; *b*, from caoutchouc; and *c*, from gutta percha.

I. 0·3454 grm. of *a* gave 0·1892 metallic silver.

II. 0·2462 grm. of *b* gave 0·1348 metallic silver.

III. 0·2514 grm. of *c* gave 0·2540 carbonic acid and 0·0422 water.

	Experiment.			Mean.	Calculation.		
	I.	II.	III.				
Carbon . .	——	——	27·6	27·6	C^{10}	108	27·4
Hydrogen .	——	——	1·9	1·9	H^6	6	1·5
Oxygen . .	——	——	——	——	O^3	64	16·3
Silver . .	54·8	54·8	——	54·8	Ag^2	216	54·8
						394	100·0

Corresponding sufficiently with the formula

$$C^{15}(H^6 Ag^2 O^2).$$

I intend to try the alternate action of bromine and sodium upon other isomers of turpentine, with a view to their conversion into cymole, or hydrocarbons isomeric with it.

On the Action of Sulphuric Acid on Caoutchine.

On adding slowly caoutchine to sulphuric acid (sp. gr. 1·845) in great excess, the latter becomes warm and the greater part of the hydrocarbon dissolves, traces of sulphurous acid being at the same time evolved. On the addition of water, the greater part of the caoutchine rises in an altered state to the surface; it is in the form of a thick adhesive fluid of the consistency of molasses. On saturating the acid solution with chalk, a very small quantity of the lime-salt of a conjugate sulphuric acid was obtained. It is excessively soluble in water, and deposits small granular crystals from a concentrated solution. Dried at 200° C. it gave the annexed results on analysis.

0·2594 grm. gave 0·0736 of sulphate of calcium; or, in per-centages,—

	Experiment.	Calculation.		
Carbon . .		C^{20}	120	51·1
Hydrogen .		H^{15}	15	6·4
Calcium . .	8·3	Ca	20	8·5
Sulphur . .		S^2	32	13·6
Oxygen . .		O^5	48	20·4
			235	100·0

From the agreement of the theoretical with the experimental numbers, the formula

$$C^{20} H^{15} Ca S^2 O^5$$

is evidently that of the substance in question.

On the Composition of Caoutchouc.

The only analyses of caoutchouc which I have seen, are those of Faraday and the late Dr. Ure. That of the latter chemist is obviously incorrect, as he obtained 90 per cent. of carbon and only 9·1 of hydrogen, a result incompatible with the phenomena which take place under the influence of heat.

Faraday's analysis, made in the year 1826, is probably almost exactly the true composition of a pure caoutchouc. It gave carbon 87·2 and hydrogen 12·8 per cent. These numbers would require to be slightly modified, in consequence of the atomic weight of carbon, as now received, having a somewhat different value to that which was admitted at the time of the analysis. I analysed two small specimens which had formed

in phials of the juice, with the annexed results. They were dried at 100°. The first specimen was dark brown, the second pale straw-coloured and almost transparent.

I. 0·2010 grm. gave 0·6346 carbonic acid and 0·2230 water.
II. 0·1972 grm. gave 0·6252 carbonic acid and 0·2134 water.
III. 0·5958 grm. gave 0·0054 of brilliantly white ash.

Or, per cent.,—

	Experiment.		Faraday.
Carbon	86·1	86·5	87·2
Hydrogen	12·3	12·0	12·8
Ash	0·9		
Nitrogen, oxygen, and loss	0·7		
	100·0		

My specimens were probably less pure than that analysed by Faraday.

I am anxious to call attention to the fact that the atomic constitution of caoutchouc appears to bear some simple relation to the hydrocarbons resulting from its decomposition by heat. The composition of caoutchouc coincides with that of isoprene and caoutchine, as found by analysis, to a degree which is remarkable when we consider that caoutchouc, in addition to being non-crystalline, is scarcely capable of purification by chemical means. Additional evidence may be found in the smallness of the residue which is left on submitting caoutchouc to heat. The following results of the analyses will show the amount of confidence which may be placed in this idea.

	Isoprene.	Caoutchine.	Caoutchouc.		
	Mean.	Mean.	Faraday.	C. G. W.*	
Carbon	88·0	88·1	87·2	86·9	87·3
Hydrogen	12·1	12·0	12·8	12·4	12·1

The following Table contains a summary of the physical properties of isoprene and caoutchine.

Table of the Physical Properties of Isoprene and Caoutchine.

Name.	Formula.	Boiling-point.	Specific gravity.	Vapour-density.	
				Experiment.	Calculation.
Isoprene	$C^{10}H^8$	37°	0·6823 at 20°	2·44	2·349
Caoutchine	$C^{20}H^{16}$	171	0·8420	4·65	4·699

It will be seen from what has been said upon the composition of the above bodies, that they may equally be obtained from caoutchouc or gutta percha. When the latter substance is submitted to careful distillation, the phenomena are essentially the same as with the former. The distillate contains a small quantity of water, which, instead of

* Ash deducted.

being alkaline, as with caoutchouc, is powerfully acid. The acid is volatile, and appears to belong to one of the lower members of the series $C^n H^n O^4$. On neutralizing the acid fluid with potash or soda, the odour of a volatile base becomes very perceptible.

The oily distillate, as with caoutchouc, consists principally of the thick uninviting fluid called by Bouchardat 'hévéène.' I have not as yet minutely examined it, but I believe it to bear a polymeric relation to caoutchine.

The amount of isoprene in the crude distillate is very small, probably not more than five per cent., and, as will readily be supposed with so volatile a fluid, much is lost in the subsequent purification. It is this circumstance which has prevented me from examining it so closely as could be desired.

The caoutchine constitutes about twenty per cent. of the distillate; it was sensibly less pure than that procured from caoutchouc, and more rectifications over sodium were necessary before it was obtained in a sufficiently pure state for analysis. This partly arises from the tenacious manner in which the volatile acids above alluded to adhere to it, and render treatment with alkalies essential previous to rectification. It is also accompanied by what we are too much accustomed to vaguely term empyreumatic products. These are of a readily oxidizable nature, and may be got rid of by rectification two or three times over hydrate of potash.

The following is a brief summary of the results of the above investigation:—

1. The isolation of isoprene, $C^{10} H^8$, the existence of which among the products of the destructive distillation of caoutchouc had not been proved.

2. The production of an apparently definite oxide of the hydrocarbon $C^{10} H^8$, by the agency of ozone spontaneously generated.

3. The determination of the polymeric relation between isoprene and caoutchine.

4. The conversion of turpentine and caoutchine into the hydruret of thymyle or cymole.

5. The production of paracymole.

6. The determination of the products of the destructive distillation of gutta percha.

XVI. *On the Relation between Boiling-point and Composition in Organic Compounds.*

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Received March 20,—Read May 3, 1860.

THE researches which I beg, in the following pages, to submit to the Royal Society, embody the results obtained in the further development of an observation which I made a considerable number of years ago, and which, since that time, I had to defend against the objections of others, both by experimental inquiries of my own, and by the collection and discussion of facts elicited in the investigations of other observers. As far back as 1841* I pointed out that in analogous compounds the same difference of composition frequently involves the same difference in boiling-points. The assertion of the existence of this law-like relation between the chemical composition of substances and one of their most important physical properties, when first enunciated, met rather with the opposition than with the assent of chemists. In Germany especially it was contested by SCHRÖDER in his memoir "On the Molecular Volume of Chemical Compounds†." These objections led me to collect additional evidence‡ in favour of my views, and to show more particularly that in very extensive series of compounds (alcohols $C_n H_{n+2} O_2$; acids $C_n H_n O_4$; compound ethers $C_n H_n O_4$, &c.) an elementary difference $xC_2 H_2$ is attended by a difference of $x \times 19°$ C. in the boiling-points, and how this fact is intimately connected with other regularities exhibited by the boiling-points of organic compounds. Almost at the same period SCHRÖDER§ convinced himself that the relation I had pointed out obtains in most cases. He collected himself a considerable number of illustrations of the regularities I had traced, and showed that the relation in question is rendered more especially conspicuous if the compounds be expressed by formulæ representing equal vapour-volumes of the several substances. Some of the views, however, which were peculiar to SCHRÖDER have not gained the approbation of chemists. This physicist was inclined to consider the boiling-point of a substance as the most essential criterion of its proximate constituents, as the most trustworthy indicator of its molecular constitution. His views were chiefly based upon the assumption that the elementary difference $C_2 H_2$, when occurring in alcohols $C_n H_{n+2} O_2$, involved a difference of boiling-points other than that occasioned by the same elementary difference obtaining in acids $C_n H_n O_4$,

* Ann. der Chem. und Pharm. vol. xlix. pp. 71 and 169.

† Ueber die Molecular-Volume der Chemischen Verbindungen, 1843.

‡ Ann. der Chem. und Pharm. vol. l. p. 128.

§ Ueber die Siedhitze der Chemischen Verbindungen, 1844.

and that the isomeric compound ethers differed from one another in their boiling-points. An extensive series of boiling-point determinations* which I made of these isomeric ethers, proved that the latter assumption is not founded on facts. The exertions made by SCHRÖDER, GERHARDT, LÖWIG and others, in the hope of recognizing the influence of the constituent elements on the boiling-point of a compound, have also essentially remained without result†.

In France the existence of the relations between composition and boiling-point which I had observed, has been contested by I. PIERRE‡, who determined the boiling-points of many organic compounds, while engaged in an inquiry regarding their expansion. In England, lastly, W. A. MILLER§ has likewise called attention to the discrepancies between the boiling-points observed by PIERRE and those calculated on the supposed existence of the relations which I had indicated. I was, however, enabled‖ to remove these apparent discrepancies by the first results obtained in a long series of experimental observations of my own, in which, at intervals and as material and opportunities presented themselves, I have continued up to the present day.

The existence of the relations between composition and boiling-point, such as it results from my original observations, has, notwithstanding these objections, been generally acknowledged. In many cases the recognition of these relations furnished important arguments in discussions regarding the true molecular value of organic compounds. Chemists have observed a vast number of new illustrations, and for several series, in which the individual terms differ from each other by a constant elementary difference, the corresponding difference of boiling-point has been carefully determined¶. Nevertheless, these relations, the important means of control which they afford in experimental inquiries, and the assistance which they are frequently capable of lending in the determination of the true chemical character of a new compound, have scarcely been sufficiently appreciated.

The rapid progress of organic chemistry has greatly expanded the material available for the discussion of boiling-points, and up to the latest date the stream of experimental inquiry, whilst confirming or correcting former observations, has furnished a rich supply of additional important facts. The time has arrived when a survey of the territory safely acquired may be taken, and when from the boundary lines reached we may fix the directions in which we have next to advance.

A collection of my researches on this subject in a connected form, permitting this survey, and showing the results which may be expected from their application, I now beg leave to submit to the Royal Society, hoping that their attention may not be with-

* Ann. der Chem. und Pharm. vol. lv. p. 166.

† In reviewing SCHRÖDER'S memoir on this subject, I have pointed out the reasons which render the general solution of this problem almost hopeless.—Pogg. Ann. vol lxxxi. p. 374.

‡ Thèse soutenue à la Faculté des Sciences à Paris (Annuaire de Chimie, par MILLON et REISET, 1846).

§ Quarterly Journal of the Chemical Society, vol. i. p. 363. ‖ Ibid. vol. iii. p. 104.

¶ The careful manner in which A. H. CHURCH (Phil. Mag. [4] ix. 256) has determined the difference of the boiling-points for the series of hydrocarbons $C_n H_{n-6}$, deserves especially to be mentioned.

held from a field where our knowledge, emanating from earlier observations, but expanded and consolidated more than ever before by recent experimental evidence, has already gained a solid foundation.

It is especially with regard to organic compounds that constant relations between boiling-point and composition have been demonstrated. It often occurs that in the case of analogous compounds the same difference in the boiling-points corresponds to the same difference in the chemical formulæ, or that the differences in boiling-points and those in composition are proportional. In different series of analogous compounds the same differences of boiling-point may correspond to the same differences of composition, but this does not obtain in all series. The regularities exhibited by the boiling-points of organic compounds, and more especially the observation of the same difference of boiling-point corresponding to the same difference of composition, are limited to certain groups. In other groups, the same difference in the formulæ involves another difference in the boiling-points.

Among the earliest recognized regularities, comprising at the same time the largest number of compounds, are the following:—An alcohol $C_n H_{n+2} O_2$, which contains $x\,C_2 H_2$ more or less than another, boils at a temperature $x \times 19°$ higher or lower. An acid $C_n H_n O_4$, boils at a temperature 40° higher than the alcohol $C_n H_{n+2} O_2$, the oxidation of which may give rise to the acid. A compound ether $C_n H_n O_4$, boils at a temperature 82° lower than the acid $C_n H_n O_4$ isomeric with it. If we start from the boiling-point of ethyl-alcohol =78°, these three propositions enable us to calculate the boiling-points of a large number of organic substances, alcohols, acids, and compound ethers, represented by the above general formulæ, as given in the following Table:—

TABLE I.

Calculated boiling-points.					
Alcohols $C_n H_{n+2} O_2$.		Acids $C_n H_n O_4$.		Compound ethers $C_n H_n O_4$.	
	°		°		°
$C_2 H_4 O_2$	59	$C_2 H_2 O_4$	99		
$C_4 H_8 O_2$	78	$C_4 H_4 O_4$	118	$C_4 H_4 O_4$	36
$C_6 H_8 O_2$	97	$C_6 H_6 O_4$	137	$C_6 H_6 O_4$	55
$C_8 H_{10} O_2$	116	$C_8 H_8 O_4$	156	$C_8 H_8 O_4$	74
$C_{10} H_{12} O_2$	135	$C_{10} H_{10} O_4$	175	$C_{10} H_{10} O_4$	93
$C_{12} H_{14} O_2$	154	$C_{12} H_{12} O_4$	194	$C_{12} H_{12} O_4$	112
$C_{14} H_{16} O_2$	173	$C_{14} H_{14} O_4$	213	$C_{14} H_{14} O_4$	131
$C_{16} H_{18} O_2$	192	$C_{16} H_{16} O_4$	232	$C_{16} H_{16} O_4$	150
$C_{18} H_{20} O_2$	211	$C_{18} H_{18} O_4$	251	$C_{18} H_{18} O_4$	169
$C_{20} H_{22} O_2$	230	$C_{20} H_{20} O_4$	270	$C_{20} H_{20} O_4$	188
$C_{22} H_{24} O_2$	249	$C_{22} H_{22} O_4$	289	$C_{22} H_{22} O_4$	207
$C_{24} H_{26} O_2$	268	$C_{24} H_{24} O_4$	308	$C_{24} H_{24} O_4$	226
$C_{26} H_{28} O_2$	287	$C_{26} H_{26} O_4$	327	$C_{26} H_{26} O_4$	245
$C_{28} H_{30} O_2$	306	$C_{28} H_{28} O_4$	346	$C_{28} H_{28} O_4$	264
$C_{30} H_{32} O_2$	325	$C_{30} H_{30} O_4$	365	$C_{30} H_{30} O_4$	283
$C_{32} H_{34} O_2$	344	$C_{32} H_{32} O_4$	384	$C_{32} H_{32} O_4$	302

The degree of accuracy with which the numbers of this Table represent the boiling-points of the several substances, may be gathered from a comparison of these numbers

with the results of observation, due attention being paid at the same time to the marked discrepancies exhibited by the several results of observation obtained in determining the boiling-point of one and the same substance.

In the following Tables I give the calculated boiling-points of a number of compounds side by side with the results of several observers:—

TABLE II.

Alcohols $C_nH_{n+2}O_2$.		Calculated.	Observed boiling-point.
		°	
Methyl-alcohol	$C_2H_4O_2$	59	Kane, 60°; Delffs, 60°·5; Kopp, 65°; Pierre, 66°; Dumas and Péligot, 66°·5.
Ethyl-alcohol	$C_4H_6O_2$	78	Dumas and Boullay, 76°; Gay-Lussac, Pierre, Kopp, Delffs, Andrews, 78°.
Propyl-alcohol	$C_6H_8O_2$	97	Chancel, 96°.
Butyl-alcohol	$C_8H_{10}O_2$	116	Wurtz, 109°.
Amyl-alcohol	$C_{10}H_{12}O_2$	135	Pasteur, 127°—129°; Cahours, Pierre, Kopp, Delffs, 132°; Rieckher, 135°.
Caproyl-alcohol	$C_{12}H_{14}O_2$	154	Faget, 148°—154°.
Œnanthyl-alcohol	$C_{14}H_{16}O_2$	173	Städeler, 177°—177°·5.
Cetyl-alcohol	$C_{32}H_{34}O_2$	344	Favre and Silbermann, 366°?.

TABLE III.

Acids $C_nH_nO_4$.		Calculated.	Observed boiling-point.
		°	
Formic acid	$C_2H_2O_4$	99	Liebig, 99°; Bineau, Favre and Silbermann, 100°; Kopp, 105°.
Acetic acid.....	$C_4H_4O_4$	118	Delffs, 116°; Kopp, 117°; Sébille-Auger, 119°; Dumas, 120°.
Propionic acid	$C_6H_6O_4$	137	Dumas, Malaguti and Leblanc, about 140°; Limpricht, Kopp, 142°.
Butyric acid	$C_8H_8O_4$	156	Kopp, Delffs, 156°; Pierre, 163°; Pelouze and Gélis, about 164°.
Valeric acid	$C_{10}H_{10}O_4$	175	Dumas and Stas, Delffs, 175°; Kopp, 176°.
Caproic acid	$C_{12}H_{12}O_4$	194	Brazier and Gossleth, Wurtz, 198°; Fehling, 202°—209°.
Œnanthylic acid	$C_{14}H_{14}O_4$	213	Städeler, 218°.
Caprylic acid	$C_{16}H_{16}O_4$	232	Fehling, 236°; Perrot, 238°.
Pelargonic acid	$C_{18}H_{18}O_4$	251	Perrot, 255°; Cahours, 260°.

TABLE IV.

Compound ethers $C_n H_m O_4$.		Calculated.	Observed boiling-point.
Formate of Methyl	$C_3 H_4 O_4$	36	Kopp, Andrews, 33°; Liebig, 36°—38°.
Acetate of Methyl	$C_4 H_6 O_4$	55	Andrews, 55°; Kopp, 56°; Dumas and Péligot, 58°.
Formate of Ethyl			Liebig, Delffs, 53°; Kopp, 55°; Löwig, 56°.
Acetate of Ethyl	$C_6 H_8 O_4$	74	Dumas and Boullay, Pierre, Kopp, Delffs, 74°.
Butyrate of Methyl ...			
Acetate of Propyl			Favre and Silbermann, Delffs, 93°; Kopp, 95°; Pierre, Berthelot, about 90°. [102°.
Formate of Butyl	$C_{10} H_{10} O_4$	93	Wurtz, about 100°.
Propionate of Ethyl ...			Kopp, 96°—98°; Limpricht and Uslar, 101°.
Valerate of Methyl ...			Kopp, 114°—115°.
Butyrate of Ethyl			Pelouze, 110°; Delffs, 113°; Kopp, 115°; Pierre, 119°.
Acetate of Butyl	$C_{12} H_{12} O_4$	112	Wurtz, 114°.
Formate of Amyl			Delffs, 114°; Kopp, about 116°.
Valerate of Ethyl			Delffs, 132°; Otto, Kopp, Berthelot, 133°—134°.
Butyrate of Propyl.....	$C_{14} H_{14} O_4$	131	Berthelot, about 130°.
Acetate of Amyl			Cahours, 125°; Kopp, Delffs, 133°.
Caproate of Ethyl	$C_{16} H_{16} O_4$	150	Lerch, 120°; Fehling, 162°.
Propionate of Amyl ...			Wrightson, about 155°.
Butyrate of Amyl	$C_{18} H_{18} O_4$	169	Delffs, 173°—176°.
Valerate of Amyl	$C_{20} H_{20} O_4$	188	Kopp, 188°; Balard, about 196°.
Acetate of Capryl			Dachauer, 191°—192°; Bouis, 193°.
Pelargonate of Ethyl...	$C_{22} H_{22} O_4$	207	Cahours, 216°—218°; Delffs, 224°.
Caproate of Amyl			Brazier and Gossleth, 211°.
Laurostearate of Ethyl ...	$C_{28} H_{36} O_4$	264	Görgey, 264°; Delffs, 269°.

There can be no doubt that if the boiling-points of other alcohols, acids, and ethers belonging to these series were correctly observed, they also would agree within a few degrees with those obtained by calculation.

The boiling-points given in Table I. are closely connected with those of other monatomic alcohols with two equivalents of oxygen, of other monobasic acids with four equivalents of oxygen, and of the ethers generated by these acids and alcohols. It is frequently observed that a compound of this kind, which, when compared with an analogous body of Table I., contains $x \times C$ more or less, boils at a temperature $x \times 14{\cdot}5$ higher or lower, or (what amounts to the same thing) that it boils at a temperature $x \times 5°$ lower or higher, accordingly as it contains $x \times H$ more or less.

Benzoic acid, $C_{14} H_6 O_4$, for example, contains 8C more than the acid $C_6 H_6 O_4$, the boiling-point of which is stated in Table I. at 137°. Consequently the boiling-point of benzoic acid will be $137 + 8 \times 14{\cdot}5 = 253$. It contains 8H less than the acid $C_{14} H_{14} O_4$, for the boiling-point of which the Table gives 213, and its boiling-point by calculation will be $213 + 8 \times 5 = 253$.

Allyl-alcohol, $C_6 H_6 O_2$, contains 2C more than ethyl-alcohol, $C_4 H_6 O_2$, which boils at 78°; the calculated boiling-point of allyl-alcohol accordingly is $78 + 2 \times 14{\cdot}5 = 107$; or it may be compared to the alcohol $C_6 H_8 O_2$, the boiling-point of which is 97° (see Table I.), when the boiling-point of allyl-alcohol, which contains 2H less, will be found by calculation $= 107$ $(= 97 + 2 \times 5)$.

The following synopsis shows in how large a number of alcohols $C_n H_m O_2$, of acids and ethers $C_n H_m O_4$, the boiling-points obey this simple rule. In perusing this Table,

it must be borne in mind that the observations of boiling-points comprised in the higher ranges of the thermometer are frequently less accurate.

TABLE V.

Alcohols $C_n H_m O_2$.		Calculated.	Observed boiling-point.
Allyl-alcohol	$C_6 H_8 O_2$	107°	Cahours and Hofmann, 103°.
Phenyl-alcohol	$C_{12} H_8 O_2$	194	Laurent, 187°—188°; Kopp, 188°.
Benzyl-alcohol	$C_{14} H_8 O_2$	213	Cannizzaro, 204°; Kopp, 207°.
Thymyl-alcohol	$C_{20} H_{14} O_2$	270	Kraut, 243°.
Styryl-alcohol	$C_{16} H_{10} O_2$	261	Wolff, 250°; E. Kopp, 254°.

TABLE VI.

Acids $C_n H_m O_4$.		Calculated.	Observed boiling-point.
Angelic acid	$C_{10} H_8 O_4$	185°	Meyer and Zenner, 190°; Reinsch, 191°.
Pyroterebic acid	$C_{12} H_{10} O_4$	204	Rabourdin, 200°; Chautard, 210°.
Benzoic acid	$C_{14} H_6 O_4$	253	Kopp, 250°.
Terebenthilic acid	$C_{16} H_{10} O_4$	262	Personne, 250°.
Cinnamic acid	$C_{18} H_8 O_4$	301	Dumas and Péligot, 293°; E. Kopp, 300°—304°.
Toluic acid	$C_{16} H_8 O_4$	272	Strecker and Möller, 266°.

TABLE VII.

Compound ethers $C_n H_m O_4$.		Calculated.	Observed boiling-point.
Acetate of Allyl	$C_{10} H_8 O_4$	103°	Cahours and Hofmann, 98°—100°; Zinin, 105°.
Butyrate of Allyl	$C_{14} H_{12} O_4$	141	Cahours and Hofmann, 140°; Berthelot, about 145°.
Valerate of Allyl	$C_{16} H_{14} O_4$	160	Cahours and Hofmann, 162°.
Acetate of Phenyl	$C_{16} H_8 O_4$	190	Scrugham, 188°.
Benzoate of Methyl	$C_{16} H_8 O_4$	190	Dumas and Péligot, Kopp, 199°.
Benzoate of Ethyl	$C_{18} H_{10} O_4$	209	Delffs, 207°; Dumas and Boullay, 209°; Kopp, 213°;
Acetate of Benzyl	$C_{18} H_{10} O_4$	209	Cannizzaro, 210°.
Toluate of Ethyl	$C_{20} H_{12} O_4$	228	Noad, 228°.
Cuminate of Ethyl	$C_{24} H_{16} O_4$	266	Gerhardt and Cahours, 240°.
Benzoate of Amyl	$C_{24} H_{16} O_4$	266	Rieckher, 252°—254°; Kopp, 261°.
Œnanthylate of Phenyl	$C_{26} H_{16} O_4$	285	Cahours, 275°—280°.
Benzoate of Allyl	$C_{20} H_{10} O_4$	238	Berthelot and Luca, 230°; Zinin, 242°.
Cinnamate of Methyl	$C_{20} H_{10} O_4$	238	E. Kopp, 241°.
Cinnamate of Ethyl	$C_{22} H_{12} O_4$	257	Marchand, 260°; E. Kopp, 262°; H. Kopp, 266°.
Benzoate of Benzyl	$C_{28} H_{12} O_4$	344	Cannizzaro, 345°.
Caprylate of Phenyl	$C_{30} H_{20} O_4$	304	Cahours, about 300°.

In all the series of analogous combinations quoted in the previous Tables, a compound containing in its formula $x\,C_3 H_2$ more than another is found to boil at a temperature $x \times 19°$ higher. The same regularity obtains in other series of analogous compounds, but by no means in all. A few other groups may also be mentioned here, in which the observed boiling-points exhibit the above regularity, at all events within the limits of uncertainty usual in boiling-point determinations. The column containing the boiling-points calculated by means of the given rule is headed by the word "assumed."

TABLE VIII.

		Assumed.	Observed boiling-point.
Trichloracetate of Methyl	$C_3\ Cl_3\ H_3O_2$	145°	Laurent, 145°.
Trichloracetate of Ethyl	$C_4\ Cl_3\ H_5O_2$	164	Leblanc, 164°.
Nitrobenzoate of Methyl	$C_{16}\ H_7\ NO_4$	279	Chancel, 279°.
Nitrobenzoate of Ethyl	$C_{18}\ H_9\ NO_4$	298	E. Kopp, 296°; Chancel, 298°.
Xanthate of Methyl	$C_4\ H_6\ O_2\ S_2$	180	Chancel, 179°.
Xanthate of Ethyl	$C_{10}\ H_{10}\ O_2\ S_2$	199	Debus, 200°.
Nitrate of Methyl	$C_2\ H_3\ NO_3$	66	Dumas and Péligot, 86°.
Nitrate of Ethyl	$C_4\ H_5\ NO_3$	85	Millon, 85°; Kopp, 86°.
Nitrate of Butyl	$C_8\ H_9\ NO_3$	123	Wurtz, about 130°.
Nitrate of Amyl	$C_{10}\ H_{11}\ NO_3$	142	Rieckher, 137°; Hofmann, 148°.
Chloride of Acetyl	$C_4\ H_3\ O_2\ Cl$	56	Gerhardt, 55°; Kopp, 55°—56°.
Chloride of Propionyl	$C_6\ H_5\ O_2\ Cl$	75	Béchamp, about 80°.
Chloride of Butyryl	$C_8\ H_7\ O_2\ Cl$	94	Gerhardt, 95°.
Chloride of Valeryl	$C_{10}\ H_9\ O_2\ Cl$	113	Béchamp, 115°—120°.
Dichloride of Ethylene	$C_4\ H_4\ Cl_2$	85	Dumas, 85°—86°; Pierre, 85°.
Dichloride of Propylene	$C_6\ H_6\ Cl_2$	104	Reynolds, 100°—103°; Cahours, 104°.
Dichloride of Butylene	$C_8\ H_8\ Cl_2$	123	Kopp, 122°; Kolbe, 123°.
Dichloride of Œnanthylene	$C_{14}\ H_{14}\ Cl_2$	180	Limpricht, 187°.
Anisol (Phenate of Methyl)	$C_{14}\ H_8\ O_2$	153	Cahours, 152°.
Phenetol (Phenate of Ethyl)	$C_{16}\ H_{10}\ O_2$	172	Cahours, 172°; Baly, 175°.
Phenamylol (Phenate of Amyl)	$C_{22}\ H_{18}\ O_2$	229	Cahours, 224°—225°.
Chloride of Benzoyl	$C_{14}\ H_5\ O_2\ Cl$	196	Malaguti, 195°; Cahours, 196°; Kopp, 198°.
Chloride of Toluyl	$C_{16}\ H_7\ O_2\ Cl$	215	Cahours, 214°—216°.
Hydride of Benzoyl	$C_{14}\ H_6\ O_2$	179	Kopp, 179°.
Hydride of Cumyl	$C_{20}\ H_{12}\ O_2$	236	Gerhardt and Cahours, 220°; Kopp, 237°.

A few other series will be mentioned in a subsequent part of this paper. Since, as I have already remarked, the regularity in question is not altogether general, it may often be doubtful whether it exists or not when the observations of the boiling-points present considerable discrepancies and uncertainties in several terms of an homologous series. As an example, the following series may be quoted:—

TABLE IX.

		Assumed.	Observed boiling-point.
Cyanide of Methyl	$C_4\ H_3\ N$	79°	Kopp, 72°; Dumas, 77°; Buckton and Hofmann, 77°—78°.
Cyanide of Ethyl	$C_6\ H_5\ N$	98	Kolbe, Meyer, 88°; Grimm, Limpricht, 98°.
Cyanide of Propyl	$C_8\ H_7\ N$	117	Dumas, Malaguti and Leblanc, 118°·5
Cyanide of Butyl	$C_{10}\ H_9\ N$	136	Schlieper, 125°; Guckelberger, 125°—128°.
Cyanide of Amyl	$C_{12}\ H_{11}\ N$	155	Frankland and Kolbe, 146°; Wurtz, 155°.

The comparison of the boiling-points of the corresponding terms in the several series of homologous substances given in the preceding Tables, exhibits several other constant differences in the boiling-points for certain differences in the formulæ. In addition

to those hitherto noticed, the following also deserve to be mentioned, since they are likewise observed in other compounds.

The foregoing Tables afford many illustrations of the facts, that the boiling-point of an acid lies 63° higher than that of the methyl-ether, 44° higher than that of the ethyl-ether, and 13° lower than that of the amyl-ether of the same acid. These regularities appear to obtain in the case of acids other than those quoted. The boiling-point of monochloracetic acid (185°—188°, R. Hoffmann) has been found about 44° higher than that of the monochloracetate of ethyl (143°·5, Willm). Starting from the boiling-point of trichloracetate of methyl (145°, Laurent), or from that of trichloracetate of ethyl (164°, Leblanc), the boiling-point of trichloracetic acid is found by calculation to be 208°. Dumas found it between 195° and 200°. From the boiling-point of monobromacetic acid, 208°, observed by Perkin and Duppa, that of the corresponding methyl-ether may be calculated at 145°, that of the ethyl-ether at 164°, and that of the amyl-ether at 221°. The results of observation are 144°, 159°, 207°. They are not, however, entirely to be relied upon, since the ethers of monobromacetic acid, and especially those possessing higher boiling-points, are partially decomposed by ebullition.

In a few substances other than acids, the substitution of C_4H_3 for H is occasionally attended by a decrease of 44° in the boiling-point; that of C_2H_3 for H by a decrease of 63°. Ordinary (ethyl) ether, $C_8H_{10}O_2$, boils at 34°, *i. e.* 44° lower than ethyl-alcohol, $C_4H_6O_2$; methyl-amyl-ether, $C_{12}H_{14}O_2$, at 72° (Williamson), *i. e.* 63° lower than amyl-alcohol, $C_{10}H_{12}O_2$. If any doubt remained as to the expediency of representing ordinary ether by the formula $C_8H_{10}O_2=(C_4H_3)(C_4H_3)O_2$, instead of the formula C_4H_5O, this observation might be of some importance; but the comparison of the boiling-points of alcohols and of so-called simple and mixed ethers, shows that the aforesaid regularity is not general, a circumstance arising from the fact of the elementary difference C_2H_2, in the series of ethers $C_nH_{n+2}O_2$, involving a difference of boiling-points other than that corresponding to the elementary difference C_2H_3 in the series of alcohols $C_nH_{n+2}O_2$.

The preceding Tables contain a great number of illustrations of the facts, that many compounds containing benzoyl ($C_{14}H_5O_2$) or benzyl ($C_{14}H_7$) boil at a temperature 78° higher than the corresponding compounds of valeryl ($C_{10}H_9O_2$) or of amyl ($C_{10}H_{11}$). The benzoyl- and benzyl-compounds, when compared with the compounds of valeryl and amyl, contain 4C more and 4H less. They boil mostly, in accordance with the rules given (page 261), at a temperature $(4\times14°{\cdot}5)+(4\times5°)=78°$ higher.

In addition to the compounds, the boiling-points of which have already been given, the following exhibit the same regularity. [The mixed acetone A is the one obtained by the distillation of a mixture of an acetate and benzoate; the acetone B is that formed by distilling an acetate and valerate. Hydride of benzyl is identical with toluol, chloride of benzyl with monochlorinated toluol.]

TABLE X.

		Observed boiling-point.
Hydride of Benzoyl	$C_{14} H_6 O_2$	Kopp, 179°.
Hydride of Valeryl	$C_{10} H_{10} O_2$	Kopp, 93°; Limpricht, 96°; Chancel, about 110°.
Chloride of Benzoyl	$C_{14} H_5 O_2 Cl$	Malaguti, 195°; Cahours, 196°; Kopp, 198°.
Chloride of Valeryl	$C_{10} H_9 O_2 Cl$	Béchamp, 115°—120°.
Mixed Acetone A	$C_{12} H_6 O_2$	Friedel, 198°.
Mixed Acetone B	$C_{12} H_{12} O_2$	Williamson, 120°.
Hydride of Benzyl	$C_{14} H_8$	Church, 104°; Deville, 108°; Gerhardt, 114°.
Hydride of Amyl	$C_{10} H_{12}$	Frankland, 30°.
Chloride of Benzyl	$C_{14} H_7 Cl$	Cannizzaro, 175°—176°.
Chloride of Amyl	$C_{10} H_{11} Cl$	Balard, Kopp, 101°; Pierre, Cahours, 102°.

This regularity does not, however, obtain in a general manner, as will be apparent by comparing the boiling-points of cyanide of phenyl (benzonitrile, FEHLING, KOPP, 191°; LIMPRICHT, 192°) and of cyanide of butyl (valeronitrile, SCHLIEPER, 125°; GUCKELBERGER, from 125° to 128°), or the boiling-points of toluidine (MUSPRATT and HOFMANN, 198°) and of amylamine (BRAZIER and GOSSLETH, 93°; WURTZ, 95°).

The boiling-points of the terms of several series which have been previously mentioned frequently almost coincide, a circumstance which furnishes a valuable means of controlling boiling-point observations. If, for example, in a series of methyl-ethers, corresponding to various monobasic acids with four equivalents of oxygen, and in the chlorides of the radicals contained in the same acids, the boiling-points be found so near to each other as is shown in the following Table,—

TABLE XI.

		Observed boiling-point.
Acetate of Methyl	$C_4 H_6 O_4$	Andrews, 55°; Kopp, 56°; Dumas and Péligot, 58°.
Chloride of Acetyl	$C_4 H_3 O_2 Cl$	Gerhardt, 55°; Kopp, 55°—56°.
Propionate of Methyl	$C_5 H_8 O_4$	Calculated, 74°.
Chloride of Propionyl	$C_6 H_5 O_2 Cl$	Béchamp, about 80°.
Butyrate of Methyl	$C_{10} H_{10} O_4$	Favre and Silbermann, Delffs, 93°; Kopp, 95°; Pierre, 102°.
Chloride of Butyryl	$C_8 H_7 O_2 Cl$	Gerhardt, 95°.
Valerate of Methyl	$C_{12} H_{12} O_4$	Kopp, 114°—115°.
Chloride of Valeryl	$C_{10} H_9 O_2 Cl$	Béchamp, 115°—120°.
Benzoate of Methyl	$C_{16} H_8 O_4$	Dumas and Péligot, Kopp, 199°.
Chloride of Benzoyl	$C_{14} H_5 O_2 Cl$	Malaguti, 195°; Cahours, 196°; Kopp, 198°.
Toluate of Methyl	$C_{18} H_{10} O_4$	Calculated, 209°.
Chloride of Toluyl	$C_{16} H_7 O_2 Cl$	Cahours, 214°—216°.

we are justified in expecting that new determinations will furnish also a more perfect coincidence of the boiling-points of the following pairs of substances:—

TABLE XII.

		Boiling-point.
Pelargonate of Methyl	$C_{20}H_{20}O_4$	Calculated, 188°.
Chloride of Pelargonyl	$C_{18}H_{17}O_2Cl$	Cahours, 220°.
Nitrobenzoate of Methyl ...	$C_{16}H_7(NO_4)O_4$	Chancel, 279°.
Chloride of Nitrobenzoyl ...	$C_{14}H_4(NO_4)O_2Cl$	Cahours, 265°—268°.
Cuminate of Methyl	$C_{22}H_{14}O_4$	Calculated, 247°.
Chloride of Cumyl.....	$C_{20}H_{11}O_2Cl$	Cahours, 258°—260°.
Cinnamate of Methyl.....	$C_{20}H_{10}O_4$	E. Kopp, 241°.
Chloride of Cinnamyl	$C_{18}H_7O_2Cl$	Cahours, 262°.

It is evident from the preceding Tables that phenyl-alcohol, acetate, œnanthylate, and caprylate of phenyl boil at a temperature 116° higher than the corresponding ethyl-compounds (phenyl contains 8C more than ethyl, $8\times14°{\cdot}5=116°$). The same difference is not observed in all corresponding phenyl- and ethyl-compounds, yet it occurs in cases other than those already mentioned, or which may be readily inferred from the regularities previously alluded to. Thus the boiling-point of iodide of phenyl (SCRUGHAM, 190°) is likewise about 116° higher than that of iodide of ethyl (PIERRE, 70°; ANDREWS, 71°; FRANKLAND, 72°). It deserves also to be noticed that the boiling-points of acetate of phenyl (SCRUGHAM, 188°) and of iodide of phenyl (SCRUGHAM, 190°) are as near to each other as those of acetate of ethyl (74°) and of iodide of ethyl (70°—72°); and that the same difference is observed between the boiling-points of iodide of phenyl (190°) and of iodide of ethyl (70°—72°) as between those of chloride of phenyl (SCRUGHAM, 136°) and of chloride of ethyl (PIERRE, 11°; THÉNARD, 12°).

The compounds of allyl contain 2 C more in their formulæ than the corresponding ethyl-compounds. The difference in the boiling-points $2\times14°{\cdot}5=29°$ occurs not only in the compounds already quoted (the alcohols, acetates, butyrates, valerates, benzoates), but also approximately at least in the cyanates (cyanate of ethyl 60°, according to WURTZ; cyanate of allyl 82°, according to CAHOURS and HOFMANN); in the iodides (iodide of ethyl 70°, according to PIERRE; 72°, according to FRANKLAND; iodide of allyl 101°, according to BERTHELOT and LUCA); in the ethyl-ethers (ordinary ethyl-ether, $C_4H_{10}O_2$, 34°; allyl-ethyl-ether, $C_{10}H_{18}O_2$, 62°·5, according to BERTHELOT and LUCA); and even in the aldehydes (acetic aldehyde, $C_4H_4O_2$, 20°, according to KOPP; 22°, according to LIEBIG and to PIERRE; acrolein, $C_6H_4O_2$, about 52°, according to REDTENBACHER). But in the case also of corresponding ethyl and allyl compounds, the difference in the boiling-points is by no means altogether constant, as is apparent from a comparison of the boiling-points of sulphocyanide of ethyl (146°, according to CAHOURS) and of sulphocyanide of allyl (143°, according to DUMAS and PELOUZE; 148°, according to WILL; 151°, according to KOPP).

If, on comparing the parallel terms of different series of compounds, we do not quite generally meet with the same difference in the boiling-points corresponding to the same

difference in composition, this fact arises from the circumstance that the same difference in the formulæ by no means involves the same difference of boiling-point in all series of homologous substances. For the series of the monatomic alcohols with two equivalents of oxygen, of the monobasic acids with four equivalents of oxygen, of the ethers to which both classes give rise, as well as for a few other series of homologous substances (see Table VIII.), the elementary difference $x\ C_2 H_2$ seems to involve a difference of boiling-point $x \times 19°$; but there are other series of homologous bodies in which the same elementary difference is positively attended by another, greater or smaller, difference of boiling-point.

This difference is greater, for example, in the series of hydrocarbons $C_n H_{n-6}$, in which it amounts to about 24°.

TABLE XIII.

Benzol.....	$C_{12} H_6$	Kopp, 80°; Mansfield, Church, 81°; Faraday, Mitscherlich, 86°.
Toluol.....	$C_{14} H_8$	Church, 104°; Deville, 108°; Noad, 110°; Gerhardt, 114°.
Xylol	$C_{16} H_{10}$	Church, 126°; Cahours, 129°.
Cumol.....	$C_{18} H_{12}$	Abel, Church, 148°; Gerhardt and Cahours, 151°.
Cymol.....	$C_{20} H_{14}$	Mansfield, Church, 171°; Gerhardt and Cahours, 175°; Kopp, 178°.

Nearly equally great is the difference in the isolated alcohol radicals $C_n H_{n+2}$.

TABLE XIV.

$C_{12} H_{14}$:—	Propyl, 68° (Williams); ethyl-butyl, 62° (Wurtz).
$C_{14} H_{16}$:—	Methyl-caproyl, 82° (Wurtz); ethyl-amyl, 88° (Wurtz).
$C_{16} H_{18}$:—	Butyl, 106° (Wurtz); 108° (Kolbe); 109° (Kopp).
$C_{18} H_{20}$:—	Butyl-amyl, 132° (Wurtz).
$C_{20} H_{22}$:—	Amyl, 155° (Frankland); 158° (Wurtz); butyl-caproyl, 155° (Wurtz).
$C_{24} H_{26}$:—	Caproyl (Brazier and Gossleth, Williams), 202°.

In the acetones and aldehydes $C_n H_n O_2$, the difference in the boiling-points corresponding to the elementary difference $C_2 H_2$ is likewise greater than 19°; the boiling-points of several of the terms of these series are, however, but very imperfectly known. Those of the acetones seem to have been the more accurately determined.

TABLE XV.

Diff.				Diff.
$2\ C_2 H_2$ ...	$C_3 H_6 O_2$ ...	Acetone	Liebig, Dumas, Kopp, 56°.....	...2×22
$2\ C_2 H_2$ ...	$C_5 H_{10} O_2$ ...	Propione	Limpricht and Uslar, 110°; Friedel, 111°	.....2×22
$6\ C_2 H_2$ ...	$C_7 H_{14} O_2$ ...	Butyrone	Chancel, about 144°; Friedel, about 145°	.....6×20
	$C_{13} H_{26} O_2$ ...	Œnanthylone	Uslar and Seekamp, 264°	

The boiling-points of the so-called simple and mixed ethers $C_n H_{n+2} O_2$ also differ by more than 19° for $C_2 H_2$. But in this series also the boiling-points of but few terms have been accurately observed. The available data, some of which will claim our attention hereafter, are the following:—

TABLE XVI.

$C_2H_6O_2$	—Methyl-ether, Berthelot, —21°.
$C_3H_8O_2$	—Methyl-ethyl-ether, Williamson, 11°.
$C_4H_{10}O_2$	—Ethyl-ether, Dumas and Boullay, Kopp, 34°; Andrews, Delffs, 35°.
$C_{12}H_{14}O_2$	—Methyl-amyl-ether, Williamson, 72°; ethyl-butyl-ether, Wurtz, 78°—80°.
$C_{14}H_{18}O_2$	—Ethyl-amyl-ether, Williamson, 112°; Guthrie, 111°—113°.
$C_{16}H_{18}O_2$	—Butyl-ether, Wurtz, 100°—104°?
$C_{20}H_{22}O_2$	—Amyl-ether, Gaultier, 170°; Wurtz, 170°—175°; Rieckher, 175°—183°.

Still greater (amounting to about 30°) is the difference in the boiling-points corresponding to the elementary difference C_2H_2 in the chlorides, bromides, and iodides of the alcohol radicals, C_nH_{n+1}. The boiling-points of the methyl, ethyl, butyl, and amyl compounds are known with tolerable certainty.

TABLE XVII.

Diff.			Diff.
C_2H_2	C_3H_3Cl	Berthelot, —20°	
			31
$2C_2H_2$	C_4H_5Cl	Pierre, +11°	
			2×31
C_2H_2	C_6H_7Cl	Wurtz (70°—75°), 73°	
			29
	$C_{10}H_{11}Cl$	Pierre, Cahours, 102°	
C_2H_2	C_3H_3Br	Pierre, 13°	
			28
$2C_2H_2$	C_4H_5Br	Pierre, 41°	
			2×24
C_2H_2	C_6H_7Br	Wurtz, 89°	
			30
	$C_{10}H_{11}Br$	Pierre, 119°	
C_2H_2	C_3H_3I	Andrews, 42°; Pierre, 44°	
			27
$2C_2H_2$	C_4H_5I	Pierre, 70°; Andrews, 71°; Frankland, 72°	
			2×25
C_2H_2	C_6H_7I	Wurtz, 121°	
			28
	$C_{10}H_{11}I$	Frankland, 146°; Kopp, 148°; Grimm, 149°	

Similar remarks apply to the sulphides $(C_nH_{n+1})_2S_2$:

TABLE XVIII.

Diff.			Diff.
$2C_2H_2$	$C_4H_6S_2$	Regnault, 41°	2×25
$6C_2H_2$	$C_{10}H_{10}S_2$	Pierre, 91°	6×21
	$C_{26}H_{22}S_2$	Balard, 216°	

Also to the Mercaptans $(C_nH_{n+1})HS_2$.

$2C_2H_2$	$C_4H_6S_2$	Liebig, 36°	2×26
C_2H_2	$C_6H_8S_2$	Humann, 88°	29—32
	$C_{10}H_{12}S_2$	Krutzsch, 117°; Kopp, 120°	

On the contrary, the difference in the boiling-points is less than 19° in the anhydrous acids (anhydrides) $C_nH_{n-2}O_6$.

TABLE XIX.

Diff.		Anhydrous.		Diff.
$2C_2H_2$	$C_9H_6O_4$	Acetic acid	Gerhardt, Kopp, 138°	.....$2\times13{\cdot}5$
$2C_2H_2$	$C_{13}H_{10}O_4$	Propionic acid	Limpricht and Ualar, 165° ...	.....$2\times12{\cdot}5$
$2C_2H_2$	$C_{15}H_{14}O_4$	Butyric acid	Gerhardt, about 190°	.....$2\times12{\cdot}5$
$2C_2H_2$	$C_{20}H_{18}O_4$	Valeric acid	Chiozza, about 215°	.....$2\times12{\cdot}5$
$6C_2H_2$	$C_{32}H_{30}O_4$	Caprylic acid	Chiozza, about 290°	.....$6\times12{\cdot}5$

In the ethers of the acids $C_nH_{n-2}O_4$, homologous to oxalic acid, the difference in boiling-point corresponding to the elementary difference C_2H_2 seems to be about 14°; this number, however, is somewhat uncertain, as boiling-points rather differing from one another have in some cases been observed for isomeric ethers. Isomeric with the latter, or belonging to the same series, are those ethers derived from the glycols $C_nH_{n+2}O_4$ by the action of two equivalents of an acid $C_nH_nO_4$. All the data respecting the boiling-points of these ethers, $C_nH_{n-2}O_4$, are collected in the following Table:—

TABLE XX.

$C_4H_4O_4$ ...	Oxalate of Methyl	Dumas and Péligot, 161°; Delffs, 164°.
$C_{10}H_{10}O_4$	Oxalate of Ethyl	Kopp, 185°; Delffs, 186°.
	Succinate of Methyl	Fehling, 198°.
	Diacetate of Ethyl-glycol	Wurtz, 186°—187°.
$C_{11}H_{12}O_4$ ...	Diacetate of Propyl-glycol	Wurtz, 186°.
$C_{16}H_{14}O_4$	Succinate of Ethyl	D'Arcet, Fehling, 214°; Kopp, 217°.
	Diacetate of Butyl-glycol	Wurtz, about 200°.
	Butyro-acetate of Ethyl-glycol ...	Simpson, 208°—215°.
$C_{18}H_{18}O_4$	Diacetate of Amyl-glycol	Wurtz, above 200°.
	Valer-acetate of Ethyl-glycol ...	Lourenço, about 230°.
$C_{20}H_{18}O_4$ ...	Dibutyrate of Ethyl-glycol	Wurtz, 239°—241°.
$C_{24}H_{22}O_4$	Suberate of Ethyl	Laurent, 260°.
	Oxalate of Amyl	Cahours, 260°; Balard, 262°.
	Sebate of Methyl	Carlet, 285°.
	Divalerate of Ethyl-glycol	Lourenço, about 255°.
$C_{26}H_{26}O_4$ ...	Sebate of Ethyl	Carlet, 308°.

The difference is also less than 19° in the carbonates, the sulphocyanides, the borates of the alcohol radicals C_nH_{n+1}, and in the bromides of the diatomic radicals C_nH_n.

TABLE XXI.

Diff.			Diff.
$4C_2H_2$	$C_{10}H_{10}O_4$	Ettling, Cahours, 125°	.....4×16
$2C_2H_2$	$C_{12}H_{12}O_4$	Wurtz, 190°	.....2×18
	$C_{22}H_{22}O_4$	Medlock, 224°; Bruce, 226°	
C_2H_2 ...	$C_4H_2NS_2$	Pierre, 133°; Cahours, 132°	 14
$3C_2H_2$	$C_7H_5NS_2$	Cahours, 146°	.....3×17
	$C_{13}H_{11}NS_2$	Henry, 195°—210°; Medlock, 197°	
$3C_2H_2$	$3C_2H_2O, BO_3$	Ebelmen and Bouquet, 78°	.....3×16
$9C_2H_2$	$3C_6H_5O, BO_3$	Ebelmen and Bouquet, 119°; Bowman, 121°	.....9×17
	$3C_{10}H_{11}O, BO_3$	Ebelmen and Bouquet, 270°—275°	
C_2H_2	$C_4H_4Br_2$	Regnault, 129°; Pierre, 133°; Cahours, 130°	 15
C_2H_2	$C_6H_6Br_2$	Reynolds, 143°; Cahours, 145°	 15
	$C_8H_8Br_2$	Wurtz, about 158°; Cahours, 160°	

There can be no doubt that in different series of homologous compounds the difference of boiling-point corresponding to the elementary difference $x\,C_2H_2$ may vary; that frequently it is found to be $x \times 19°$, but sometimes more, sometimes less. As to these inequalities of differences, they are sure to be governed by a more general law, which will probably be recognized when a sufficient number of boiling-points shall have been determined under a pressure different from the ordinary pressure of the atmosphere; for it cannot by any means be taken for granted that two substances will exhibit the same difference of boiling-point, whatever may be the pressure. Let S and S_1 be the boiling-points of two liquids under the ordinary pressure, and s and s_1 the boiling-points under another pressure. Then the assumption of $S-S_1=s-s_1$ would involve the inference $S-s=S_1-s_1$; *i. e.* that the boiling-points must undergo precisely the same change for the same change of pressure. But this conclusion, the so-called law of Dalton, is by no means correct; and it may be legitimately held that the homologous substances which under the ordinary pressure do not exhibit the most frequently observed difference of boiling-point (19°) for the elementary difference C_2H_2, would certainly show that difference under a different pressure.

Sufficient data are still wanting for the appreciation of the mode in which differences in boiling-points are affected by changes of pressure. But the extent of these alterations may in a measure be inferred from the fact that the difference in boiling-points of alcohol and ether, which, under the ordinary pressure, amounts to about 44°, from what is known with respect to the vapour-tension of these two substances at different temperatures, would, under the pressure of half an atmosphere, be above 45°, and below 40° under a pressure of three atmospheres.

From the observations at present at our disposal, it may be affirmed as a general rule, that in homologous compounds belonging to the same series, the differences in boiling-points are proportional to the differences of the formulæ. Exceptions obtain only in cases in which terms of a particular group are rather difficult to prepare, or when the substances boil at a very high temperature, at which the observations now at our command are for the most part uncertain. Again, it may be affirmed that the difference in boiling-points corresponding to the elementary difference C_2H_2, is in a great many series $=19°$; in some series more, in some series less.

There are a few quite exceptional cases in which the higher terms of a homologous series boil at a lower temperature than the inferior terms. A case in point exists according to Wurtz in the glycols.

Table XXII.

Ethyl-glycol	$C_4H_6O_4$	197°—$197^{\circ}{\cdot}5$; Atkinson, 198°.
Propyl-glycol	$C_6H_8O_4$	188—189
Butyl-glycol	$C_8H_{10}O_4$	183—184
Amyl-glycol	$C_{10}H_{12}O_4$	177

The ethers which arise from the combination of these bodies with acids $C_n H_n O_4$, exhibit on the other hand boiling-points rising with the increasing number of carbon-atoms. And this remark applies not only to those ethers of the glycols which contain two molecules of an acid-radical (compare Table XX.), but also to those in which only one of the two basic hydrogen equivalents of ethyl-glycol is replaced by an acid-radical.

TABLE XXIII.

$C_6 H_8 O_4$	Monoacetate of Ethyl-glycol	Atkinson, 188°.
$C_{12} H_{12} O_4$	Monobutyrate of Ethyl-glycol	Lourenço, about 220°.
$C_{14} H_{14} O_4$	Monovalerate of Ethyl-glycol	Lourenço, about 240°.

One more example of a compound exhibiting a boiling-point lower than that of its lower homologue is offered by the cyanurates of methyl and ethyl. According to WURTZ's earlier experiments, cyanurate of methyl, $C_{12} H_9 N_3 O_6$, boils at 295°; according to a later observation, at 274°; cyanurate of ethyl, $C_{18} H_{15} N_3 O_6$, according to the earlier observation, at 276°; according to the later, at 253°. The boiling-points of the cyanic ethers, on the other hand, rise with the increase of the number of carbon-atoms; cyanate of methyl, $C_4 H_3 N O_3$ (boiling-point 40°, WURTZ), and cyanate of ethyl, $C_6 H_5 N O_3$ (boiling-point 60°, WURTZ), exhibit the difference of boiling-points usual in this kind of ethers.

Isomeric compounds belonging to the same type, and possessing the same chemical character, have the same boiling-point. This seems to follow from the boiling-points, such as have been observed for isomeric ethers $C_n H_n O_4$ (Table IV.); for ethers $C_n H_{n-8} O_4$ and $C_n H_{n-10} O_4$ (Table VII.); and for so-called simple and mixed radicals $C_n H_{n+2}$ (Table XIV.). Boiling-points, which at any rate very nearly approach each other, have also been observed for the isomeric ethers $C_n H_{n+2} O_2$ (see Table XVI.). For the isomeric ethers $C_n H_{n-2} O_2$, observation has hitherto yielded boiling-points which sometimes agree, sometimes differ. As yet no sufficient grounds exist for attributing different boiling-points to isomeric compounds of the same type and the same chemical character. It may sometimes be difficult experimentally to prove the identity of the boiling-point of two such compounds as an ethyl-ether and the isomeric methyl-compound. The methyl-compounds have in general so great a tendency to boil irregularly, and at temperatures anomalously raised, that quiet ebullition permitting the observation of the correct boiling-point is often scarcely to be attained.

Isomeric compounds belonging to the same type, but possessing a different chemical character, have different boiling-points. This is evident, *e. g.*, from a comparison of the acids and ethers $C_n H_n O_4$ (Tables III. and IV.); of the acids and ethers $C_n H_{n-2} O_4$, $C_n H_{n-8} O_4$, or $C_n H_{n-10} O_4$ (Tables VI. and VII.); of the alcohols and ethers $C_n H_{n+2} O_2$ (Tables II. and XVI.); of the mercaptans and the sulphur-compounds isomeric with them $C_n H_{n+2} S_2$ (Table XVIII.).

Isomeric compounds belonging to different types have different boiling-points. Allyl-

alcohol, $C_6H_8O_2$, boils (Cahours and Hofmann) at 103°. (From Table V. this boiling-point was calculated at 107°.) Acetone, $C_6H_6O_2$, isomeric with the former, boils at 56° (Liebig, Dumas, Kopp).

In cases like the last, the determination of the boiling-point of a compound, together with an examination of the substances with which the compound is serially allied in boiling-point, may be of great assistance in fixing its character, the type to which it belongs, and the series of homologous bodies of which it is a term. The examples just quoted of the fact that isomeric substances of different series possess different boiling-points, may here again serve as illustrations. The boiling-point of the so-called eugenic acid (Brüning, 248°; Williams, 251°) shows that this substance, although represented by the formula $C_{20}H_{12}O_4$, cannot possibly be homologous to benzoic acid, $C_{14}H_6O_4$ (boiling-point observed by Kopp, 250°; calculated, Table VI., 253°). This result might be inferred with the greatest probability from the boiling-point of the two substances, even if cuminic acid, isomeric with eugenic acid, and the homologue of benzoic acid, were not known. On the other hand, when the boiling-points of eugenic acid and of hydride of salicyl, $C_{14}H_6O_4$ (boiling-point 196°, Piria), are considered, it becomes extremely probable that these two bodies are homologous. (To the difference in composition, $C_6H_6=3C_2H_2$, corresponds in this case the difference in boiling-points $250-196=54=3\times18°$.)

The boiling-points of polymeric compounds are also different, and may serve to determine the formula representing a substance.

Among the isomeric compounds, in the narrower sense of the word, acids and ethers (of the common formula $C_nH_nO_4$, for example), or alcohols and ethers (of the common formula $C_nH_{n+2}O_2$, *e. g.*), exhibit in all their bearings an essentially different character. Less striking is the difference of chemical character in the various volatile bases; and it is only since the last ten years that distinctive features have been traced in several classes of these bases, which have accordingly been subdivided into primary, secondary, and tertiary monamines. The basic character possessed by all these substances has induced many to compare their boiling-points also, without duly considering to which of the several classes they might belong. But in this case, again, a comparison of boiling-points is admissible only for such bases as belong to one and the same of the above-mentioned classes. The same formula, $C_{10}H_{13}N$, represents amylamine, propyl-ethylamine, and methyl-diethylamine; but of these three bases, only the first can be compared, as to boiling-point, with methylamine and ethylamine as a true homologue. The three isomeric bases above mentioned have indeed different boiling-points, just as ethyl-alcohol and methyl-ether, isomeric compounds (both $C_4H_6O_2$), have different boiling-points. We may, however, expect that methyl-propylamine and diethylamine, both isomeric bases of the same chemical character (both secondary monamines), will have the same boiling-point, just as in the case of the isomeric ethers of the same chemical character, propionate of methyl and acetate of ethyl.

Homologous bases of the common formula $C_nH_{n-3}N$ appear to exhibit, at least approximately, for a difference in the formulæ $=xC_2H_2$ a difference in boiling-points

$=x\times19°$. The temperatures of ebullition quoted in the following Tables under the head "assumed," thus calculated, pretty nearly coincide with the results of observation.

Primary monamines:

TABLE XXIV.

		Assumed.	Observed boiling-point.
$C_{12}H_7N$	Aniline	179°	Hofmann, 182°; Kopp, 185°.
$C_{14}H_9N$	Toluidine	198	Muspratt and Hofmann, 198°.
$C_{16}H_{11}N$	Xylidine	217	Church, 213°—214°.
$C_{18}H_{13}N$	Cumidine	236	Nicholson, 225°.
$C_{20}H_{15}N$	Cymidine	255	Barlow, about 250°.

Secondary monamines:

TABLE. XXV.

		Assumed.	Observed boiling-point.
$C_{14}H_9N$	Methyl-aniline	185°	Hofmann, 192°.
$C_{16}H_{11}N$	Ethyl-aniline	204	Hofmann, 204°.
$C_{18}H_{13}N$	Ethyl-toluidine	223	Morley and Abel, 217°.
$C_{20}H_{15}N$		242	
$C_{22}H_{17}N$	Amyl-aniline	261	Hofmann, 258°.

Tertiary monamines:

TABLE XXVI.

		Assumed.	Observed boiling-point.
$C_{10}H_5N$	Pyridine	115°	Anderson, 115°.
$C_{12}H_7N$	Picoline	134	Anderson, 135°.
$C_{14}H_9N$	Lutidine	153	Anderson, 154°; Williams, 160°—165°.
$C_{16}H_{11}N$	Collidine	172	Anderson, 179°; Williams, 179°—182°.
$C_{18}H_{13}N$		191	
$C_{20}H_{15}N$	Diethyl-aniline	210	Hofmann, 213°·5.
$C_{22}H_{17}N$	Diethyl-toluidine	229	Morley and Abel, 229°.
$C_{24}H_{19}N$		248	
$C_{26}H_{21}N$	Ethyl-amyl-aniline	267	Hofmann, 262°.

The isomeric bases $C_nH_{n-5}N$, belonging to different classes, have different boiling-points. The discrepancies are by no means great in the case of the isomeric terms of the primary and secondary monamines, but considerable enough in the case of the tertiary monamines compared with the two previous classes, so that the bases belonging to the third class may be distinctly recognized. Dimethylaniline may be expected to exhibit the same boiling-point as collidine, isomeric with it, and likewise a tertiary monamine.

The relation mentioned (page 261), viz. that for certain classes of alcohols, acids and ethers, a boiling-point $x\times14°{\cdot}5$ higher or lower corresponds to x C more or less in the formula, is in general not observed on comparing the bases of the first and second class; but the boiling-points of a large number of tertiary monamines, such as they are calculated from the (assumed) boiling-points of the last Table, coincide tolerably well with the results of observation.

TABLE XXVII.

		Calculated.	Observed boiling-point.
$C_{13}H_{19}N$	Methyl-piperidine	104°	Cahours, 117°.
$C_{14}H_{21}N$	Ethyl-piperidine	123	Cahours, 128°.
$C_{20}H_{31}N$	Amyl-piperidine	180	Cahours, 186°.
$C_{12}H_{19}N$	Methyl-ethyl-amylamine	132	Hofmann, 135°.
$C_{19}H_{21}N$	Diethyl-amylamine	151	Hofmann, 154°.
$C_{30}H_{33}N$	Triamylamine	265	Hofmann, 257°.

Accordingly in the last two series also the difference in boiling-point (19°) seems, at all events approximately, to correspond to the elementary difference C_2H_3. We meet, however, with an exception in the boiling-point of trimethylamine, C_6H_9N, a base likewise belonging to the tertiary monamines, which, according to WINKLES, lies between 4° and 5°*.

The general formula $C_nH_{n+3}N$ represents volatile bases of the three classes. What is known with regard to the boiling-points of the tertiary monamines has already been stated. With respect to the secondary, HOFMANN's determination of the boiling-points of diethylamine, $C_6H_{11}N$, =57°·5, of diamylamine, $C_{20}H_{23}N$, = about 170°, also exhibits for the difference of composition $x\,C_2H_3$, a difference in boiling-points of 19° (170−57=6×19°). The difference is greater for the primary bases $C_nH_{n+3}N$; the boiling-points assumed in the following Table are based on the supposition that it equals 25°.

TABLE XXVIII.

		Assumed.	Observed boiling-point.
C_2H_5N	Methylamine	− 6°	Wurtz, about 0°.
C_4H_7N	Ethylamine	+19	Wurtz, 19°.
C_5H_9N		44	
$C_6H_{11}N$	Butylamine	69	Wurtz, 69°—70°.
$C_{10}H_{13}N$	Amylamine	94	Brazier and Gossleth, 93°; Wurtz, 95°.
$C_{10}H_{15}N$		119	
$C_{14}H_{17}N$		144	
$C_{16}H_{19}N$	Caprylamine	169	Squire, 164°; Cahours, 172°—175°.

In the case of the bases $C_nH_{n+3}N$, it does not appear that the isomeric terms belonging to the classes of secondary and tertiary monamines can be distinguished by means

* The trimethylamine used by M. WINKLES, in determining the boiling-point, had been prepared from the brine of salted herrings. Whilst Professor KOPP's paper was passing through the press, I had an opportunity of determining the boiling-point of perfectly pure trimethylamine, prepared by the action of potassa on iodide of tetramethylammonium. This determination, made with about 10 grms. of base, gave the boiling-point 9°·3. The ebullition of trimethylamine exhibits the irregularity so frequently observed in methyl-compounds. When the liquid ceases to boil freely, the thermometer is observed to indicate as much as 14° and even 15°, but the mercury falls again suddenly to 9°·3, when ebullition recommences. It deserves to be noticed, that trimethylphosphine exhibits a similarly discrepant boiling-point. The boiling-point of trimethylphosphine was found between 40° and 42°, that of triethylphosphine being 127°·5.—A. W. H.

of their boiling-points; but the boiling-points of the primary monamines greatly differ from those of the isomeric bases of the two previous classes.

Constant relations then between the boiling-points and the formulæ of the volatile organic compounds may be said to have been most positively established by the preceding statements. Their existence cannot be called in question on account of their not always being manifested exactly in the same manner. Such uniformity would obtain if in all homologous series the difference in boiling-points corresponding to the difference of composition C_2H_2 were equally great; if, as a general rule, on comparing two corresponding pairs of compounds the same difference in composition were found to involve the same difference in boiling-point. The fact of these relations obtaining in a less general and simple manner renders their perception, as also their use in determining the formulæ of chemical compounds, more difficult, but does not set them aside, any more than the existence of a relation between chemical composition and crystalline form could be denied, on account of its not always manifesting itself in the simplest form, or the assistance be doubted, which the study of crystalline form often renders in establishing the formula of a substance, because compounds of altogether different atomic constitution may possess the same form, or compounds of analogous constitution, even containing so-called isomorphous elements, are observed to crystallize in forms altogether different.

Relations between boiling-point and composition have been more especially proved in organic compounds; very many of them, being volatile at comparatively low temperatures, admit of their boiling-point being accurately determined. It is, however, in the nature of the case that they should not be limited to the domain of organic chemistry. Nevertheless relations of this description have not hitherto been comprehensively proved to exist in inorganic bodies. Tribromide of arsenic, $AsBr_3$ (boiling-point 220°), and trichloride of arsenic, $AsCl_3$ (133°), exhibit nearly the same difference as oxybromide of phosphorus, PO_2Br_3 (195°), and oxychloride of phosphorus, PO_2Cl_3 (110°), and also nearly the same as the following organic compounds (exhibiting a similar difference in their formulæ), bromoform, C_2HBr_3 (152°), and chloroform, C_2HCl_3 (62°). In these cases the substitution of 3 Br for 3 Cl is attended by an elevation of the boiling-point amounting to from 85° to $90° = 3 \times 28$ to 3×30. But the substitution of x Br for x Cl by no means involves invariably an elevation of the boiling-point of from x 28° to x 30°. Although earlier observations had pointed to these simple relations, and raised the hope that a knowledge of the differences in the boiling-points of corresponding bromine and chlorine compounds would be available for ascertaining how many equivalents of bromine in a substance are substituted for chlorine in another, yet the determination of the boiling-points of a very large number of corresponding bromine and chlorine compounds has unmistakeably shown that so simple a relation does not obtain, and cannot therefore throw any light upon the formulæ of such substances.

The recognition then of definite relations between composition and boiling-point is for the present chiefly limited to organic compounds. For the majority of these com-

pounds, and indeed for the more important ones, this relation assumes the form of a simple law, which, more especially for the monatomic alcohols $C_n H_m O_2$, for the monobasic acids $C_n H_m O_4$, and for the compound ethers $C_n H_m O_4$, generated by the union of the two previous classes, is proved in the most general manner; so much so, indeed, that in many cases the determination of the boiling-point furnishes most material assistance in fixing the true character and position of a compound. And it deserves more especially to be noticed, that the simplest and most comprehensive relations have been recognized for those classes of organic compounds which have been longest known and most accurately investigated; and that even for those classes, the generality and simplicity of the relation, on account of numerous boiling-points incorrectly observed at an earlier date, appeared in the commencement doubtful, and could be more fully acknowledged only after a considerable number of new determinations. Thus we are justified in hoping that in other classes also of compounds in which simple and comprehensive relations have not hitherto been traced, these relations will become perceptible as soon as the verification of the boiling-points of terms already known, and the examination of new terms, shall have laid a broader foundation for our conclusions.

XVII. *On the Occurrence of Flint-implements, associated with the Remains of Animals of Extinct Species in Beds of a late Geological Period, in France at Amiens and Abbeville, and in England at Hoxne.* By JOSEPH PRESTWICH, *F.R.S., F.G.S. &c.*

Received May 19,—Read May 26, 1859*.

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(Maps, Sections, and Figures. Plates X. to XIV.)

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§ 1. INTRODUCTORY REMARKS.

FEW strata have been more extensively worked than the superficial sands, clays, gravels, and brick-earth belonging to the Drift or Pleistocene series, and a great number of cave-deposits belonging to the same period have also been carefully explored; nevertheless it is only in a few exceptional cases that the remains of man or of his works have been recorded as occurring in association with the mammalian and other organic remains so often found in such situations, and even these few exceptions have generally been viewed with doubt or else entirely rejected. The conclusion, in fact, that man did not exist until after the latest of our geological changes and until after the dying out of the great extinct mammals, had become almost a point of established belief†. Although resting mainly upon negative evidence and preconceived opinion, this prevalent belief was strengthened by the failure of the many ill-observed and dubious cases which had, from time to time, been brought forward. Owing to these circumstances there is little doubt that cases really meriting inquiry have been neglected or overlooked. To name only a few highly probable instances:—

In 1833, Dr. SCHMERLING‡ of Liége discovered in some caves in the valley of the Meuse, and at elevations of about 200 feet above the river, some bones of man associated with others of recent and extinct mammals: and he further subsequently

* Subsequently revised by the author, but without altering the essential facts, or extending the conclusions, of the original paper.

† Still the doctrine of the co-existence of man and of the great extinct pachyderms had been for some years partly accepted and taught by a few scientific men both in England and on the Continent.

‡ Recherches sur les Ossemens fossiles découverts dans les Cavernes de la Province de Liége. Liége, 1833–36, vol. i. p. 52–66, and vol. ii. p. 176–179.

recorded the occurrence, under the same conditions, both of worked flints and of worked bones. Amongst the human remains were two skulls, one of which, found at a depth of 5 feet in the cave-earth, "was surrounded on all sides by teeth of *Rhinoceros*, *Horse*, *Hyæna*, and *Bear*:" the other was lying at the bottom of the deposit by the side of a tooth of an *Elephant*. The human bones, like those of the extinct animals, were mostly broken and fragmentary. They were all of the same colour and mixed together indiscriminately; and, according to Dr. Schmerling, there were no traces of the ground having, in those places, been artificially disturbed.

Several remarkable instances have been recorded in Germany, whilst in France the subject has from time to time found zealous inquirers*, and some important cases are still undergoing investigation.

About thirty years ago the Rev. Mr. M'Enery, a Roman Catholic clergyman residing near Torquay, diligently explored the large and extensive cavern known as Kent's Hole, one mile east of Torquay. In the red loam, under the stalagmite floor, he found the bones of the *Mammoth*, *Tichorhine Rhinoceros*, *Cave Bear*, *Cave Hyæna*, *Horse*, &c.; whilst he also noticed, that, besides the remains of man with charred wood, and coarse pottery found scattered *on* the surface of the stalagmite, there also occurred in this red loam *under* it (though he himself seems to have doubted how far in true association with the remains of the extinct animals) worked flints of rude forms, and which he supposed to have been used as arrow-heads and knives. It was his intention to have published an account of his observations, with plates of the organic remains, and he had already, in conjunction with the late Dr. Buckland, had seventeen quarto plates engraved, when his untimely death deprived science of the result of his valuable researches. For many years it was supposed that Mr. M'Enery's MSS. were lost. A large portion of them, together with the plates, have been, however, recently recovered and published†, furnishing, although incomplete, an important addition to the history of cave-remains. On one of his plates (T, figs. 11, 12) are drawings of two flint-implements of larger size than the others, and approaching closely in form to the common Abbeville type (Plate XII. fig. 1), but the particulars concerning them are unfortunately missing. Mr. M'Enery's observations were shortly afterwards confirmed by an able and experienced geologist Mr. Godwin-Austen, who described the cave in his paper on the "Geology of South Devon," published in 1840‡. In 1847 the Torquay Natural History Society determined on a further examination of the cavern, with the special object of determining the exact

* The number of alleged cases in the South of France is not inconsiderable. For full information upon many of these and on caverns in general, I beg to refer to the work of the indefatigable and veteran geologist, M. Marcel de Serres, 'Essai sur les Cavernes à Ossemens et sur les causes qui les y ont accumulés.' Paris, 1838. See also the valuable paper on Caves (*Grottes*) by M. Desnoyers in C. D'Orbigny's 'Dictionnaire d'Histoire Naturelle,' where the question is discussed at length and with much ability. Of three alternatives this author suggests, he is disposed to adopt for the present the one which refers the association of the bones of man and of the extinct mammals to disturbances and mixture of the beds subsequent to their original separate deposition.

† Cavern Researches by the Rev. Mr. M'Enery, edited by E. Vivian, Esq. London, 1859.

‡ Transactions of the Geological Society, 2nd ser. vol. vi. p. 444.

position of these flint-implements. After taking every care to avoid error, the conclusion these gentlemen arrived at was, that, although it appeared to them that the cave had been inhabited by man at a comparatively recent period, his remains of this latter date were distinct and confined to near the surface or to the upper part of the stalagmite, whilst certain flint arrow-heads of an anterior period were certainly found in the red loam, containing the bones of extinct animals, which underlies the stalagmite.

Such instances might be multiplied, but this at present is not my object. I now wish to draw attention to the particular and remarkable case which has led to this communication, and to give the geological evidence bearing upon the question.

In the year 1841, M. Boucher de Perthes, of Abbeville, an antiquary distinguished by his varied researches, his large and valuable collections, and by an indefatigable zeal and perseverance, discovered*, in some sand with mammalian remains from the village of Menchecourt, near Abbeville (Plan A, Plate X.), a flint rudely fashioned into a cutting instrument, somewhat resembling the old flint weapons known by the name of celts, yet having a peculiar type of its own; shortly afterwards two other specimens (each above 8 inches long) were brought to him, and subsequently a considerable number have been, from time to time, obtained from the same locality. In 1844 some excavations near the hospital of Abbeville exposed a fresh section of the drift. Following up the work, M. de Perthes discovered, at various depths of from 9 to 16 feet, in a bed of sand and gravel, from which he obtained specimens of the teeth of the *Elephas primigenius*, several flints more or less worked; and on the 7th of August the workmen found at a depth of 14 feet 4 inches a still more perfect specimen, $6\frac{3}{4}$ inches long by $2\frac{3}{4}$ broad,—a fact he had certified by an official "procès-verbal" (p. 263). At the end of 1844 similar discoveries were made at Moulin Quignon; and at a later period M. de Perthes obtained specimens of the same character from Mautort, Mareuil, Drucat, and St. Riquier, in the neighbourhood of Abbeville; while at Abbeville itself some excavations at the Champ de Mars furnished a much larger number of specimens. An account of these discoveries and of his general investigations was published by M. Boucher de Perthes in 1847, in a work entitled 'Antiquités Celtiques et Antédiluviennes†,' in which he announced his belief that the flint-implements occurred in beds of undisturbed sand and gravel in true association with the bones of extinct animals. This work abounds in illustrations; and sections of the beds, drawn by Dr. Ravin, a most competent geologist, are given to show the position in which the flint-implements were found; while the evidence regarding this singular occurrence of worked flints was conscientiously discussed by the author, who concluded that they were the work of man, and that they were entombed, together with the remains of the great mammals, by the Deluge.

In 1854, Dr. Rigollot‡ of Amiens, whose attention had been directed to the subject

* The possibility of such discoveries is stated by M. B. de Perthes to have occurred to him as early as 1826, and he broached the question in his work 'Sur la Création' (Antiq. Celt. et Antéd. vol. ii. p. 359–61).

† The work was originally published in 1846, under the title of "De l'Industrie primitive." A second volume of the "Antiquités" was published in 1857. Paris: Treuttel et Wurtz.

‡ Mémoire sur des Instruments en Silex trouvés à St. Acheul près d'Amiens. Amiens, 1855.

by M. DE PERTHES' discoveries, ascertained that similar flint-implements were often found in a bed of gravel at St. Acheul near that city. He, also, after careful inquiry, expressed his conviction that the ground was undisturbed, and that these works of man were contemporaneous with the remains of the associated extinct animals. His paper contains an interesting account of the pits, with careful sections and good drawings of the worked flints, and the geological questions are more fully discussed.

These observations did not, however, attract the attention they deserved, and, with few exceptions, the discovery of M. BOUCHER DE PERTHES remained unknown to, or was considered inconclusive by, antiquaries and geologists both in France and England.

The question was in this state when attention was again directed to it by the eminent palæontologist Dr. FALCONER*, and received especially a fresh impulse by his discovery of flint-implements associated with the bones of extinct animals in Brixham Cave,—then in course of exploration at his instigation under the auspices of the Royal Society,—a fact announced by Mr. PENGELLY to the British Association in 1858. As the report on this important inquiry has not yet been presented to the Royal Society, I now merely mention this fact, to instance the weight such evidence, so carefully worked out, had in modifying previously received and generally entertained views, and in inciting further research.

It was not, however, until I had myself witnessed the conditions under which these flint-implements had been found at Brixham, that I became fully impressed with the validity of the doubts thrown upon the previously prevailing opinions with respect to such remains in caves. At the same time, although I now felt more satisfied, from the strength of the concurrent testimony and from my own observation, that these works of man did actually occur in true association with the remains of extinct mammalia in ground not artificially disturbed, still a doubt was left on my mind as to their contemporaneity. For let us suppose, first, a cave into which the bones of the extinct animals were introduced and imbedded in the red clay or loam; secondly, that the mass was then sealed up, as it were, by a layer of stalagmite; thirdly, that man afterwards frequented the cave, strewing the stalagmitic floor with his works. If, then, from any natural cause,—such for example as earthquake movements, the influx of a body of water, or any other cause tending to disturb the cave,—the stalagmite floor became broken up and the whole ground moved afresh, we might have the remains of the two periods commingled and covered up in process of time by a fresh coating of stalagmite. I would not offer this as a sufficient explanation in many cases†; but that it is a possible

* Dr. FALCONER's important researches in Sicily during the winter of 1858–59 still further stimulated inquiry. In a communication made to the Geological Society on the 4th of May 1859, an account is given of the "Grotta di Maccagnone" near Palermo, in which, besides an abundance of the remains of the *Hippopotamus* and *Elephant*, mixed with recent species of *Helix*, Dr. FALCONER announced the discovery, in portions of the same bone breccia, of small flint-implements resembling in form the obsidian knives from Mexico and the flint knives found in the old barrows of this country.—Quart. Journ. Geol. Soc. vol. xvi. p. 99.

† For another explanation see Mr. Babbage's "Observations on the Discovery in various Localities of the Remains of Human Art mixed with the Bones of Extinct Races of Animals," Proceedings of the Royal Society, May 1859, vol. x. p. 59.

case, is evident from the fact that in some caves pieces of a broken stalagmite floor are actually mixed up with bones of the animals in the loam or clay under a second and newer floor of stalagmite*.

To clear up my doubts, I resolved to take an early opportunity of examining an open section I had long intended to visit in consequence of its interest in a purely geological point of view, but now more particularly attractive in connexion with the important question raised by M. Boucher de Perthes. This section, which is exposed in digging for sand and loam at Menchecourt near Abbeville, is noted for its fossil remains of *Elephant, Rhinoceros*, &c., which are there found associated not only with many *land* and *freshwater shells*, but also with several species of *marine shells*. It has been described both by M. Ravin† and M. Buteux‡, in their excellent memoirs on the Geology of the Department. In a note to his description, M. Buteux adds that M. Boucher de Perthes had discovered hatchets and other implements in flint in the same beds, but that "this discovery may be classed with others of the same sort the exactitude of which has been contested," &c.,—a verdict generally concurred in at the time§.

The subsequent publication of Dr. Rigollot's interesting memoir again led to further discussion and inquiry by several eminent French geologists, especially M. Hébert and M. Buteux, who now frankly stated the facts relating to the discovery, but without indorsing them with the sanction of their authority or expressing any decided opinion‖. There could not have been more fitting and able geologists than these, my colleagues of the French Geological Society, to conduct any such inquiry, and I might well have left the matter entirely in their hands had they pursued the investigation further. The subject, however, seemed neglected, and no further steps, that I am aware of, were being taken to investigate it.

In the autumn of 1858 Dr. Falconer, in passing through Abbeville, examined M. Boucher de Perthes' collection, and satisfied that the flints (the *Haches*) were really worked by man, and bore all the impress of age, and that M. De Perthes had probably taken a correct view of their geological position, he wrote me a letter describing the great interest of the collection, and urging me warmly to visit the district, and to see the sections described by M. De Perthes. Feeling the desirability, in a question of this importance, of having the testimony of several competent witnesses, I proposed a visit, last Easter, to Abbeville and Amiens to some fellow members of the Geological Society, with the intention of drawing up a joint report on the subject. Owing, however, to an

* This occurs, amongst other places, in some of the caves near Liége. *Op. cit.* vol. i. pp. 19, 29, 35.

† "Mémoire Géologique sur le Bassin d'Amiens," in the Mémoires de la Société Royale d'Emulation d'Abbeville, 1834 et 1835, p. 197.

‡ Esquisse Géologique du Département de la Somme, p. 76. Amiens, 1849.

§ The non-acceptance of the same fact by M. le Viscomte d'Archiac, in his elaborate and most valuable 'Histoire des Progrès de la Géologie,' vol. ii. p. 166, and by Dr. Mantell, in his paper 'On the Remains of Man and Works of Art imbedded in Rocks and Strata,' 1851, shows how unsatisfactory the evidence was at that time considered.

‖ Bulletin de la Société Géologique de France, 2nd ser. vol. xii. p. 112 and 254. Mém. Soc. Impériale d'Emulation d'Abbeville for 1857, p. 570.

unavoidably short notice, I had to start alone, although I was afterwards joined by my friend Mr. John Evans, F.S.A.*

Thus the inquiry had not the advantage of all the co-operation for which I had hoped; nor was I more fortunate in Paris, for my friends there, upon whom I called in the hope that they might join me, were absent in the country. On my arrival at Abbeville, M. Boucher de Perthes at once accompanied me to the several localities he had described, opened his interesting collection for examination at my leisure, and placed me in full possession of all the facts bearing upon his discoveries. To M. Marcotte, Curator of the excellent local Museum of Abbeville, I am indebted for information on many points respecting the organic remains and the recent fauna of the district. To some members of the engineers "des Ponts et Chaussées" I have to express my obligations for the various levels taken through the instrumentality of M. Boucher de Perthes. At Amiens I was most kindly assisted in the furtherance of this investigation by M. Charles Pinsard, a Member of the "Société des Antiquaires de Picardie," who liberally placed at my disposal a small but special collection of teeth and bones he had found at St. Acheul, and obligingly undertook the determination of several levels which were not given on the Ordnance Maps of that district. See Appendix (F).

§ 2. SECTIONS AT ABBEVILLE AND AMIENS.

Abbeville and Amiens are both situated in the valley of the Somme, the first at a distance of about fourteen miles, and the second of forty-one miles, from the sea. The surrounding district consists of gently undulating elevated plains of chalk, capped here and there by outliers of tertiary strata, and elsewhere partly bare and partly covered by a few feet of fine light red or yellow loam and clay, in places mixed with angular fragments of flints. The river valleys are narrow, often exhibit on their flanks thick deposits of loam and gravel, while the middle is usually a flat level of marsh and peat† overlying gravel. The loam, brick-earth, or loess forms a very marked feature in this usually bare chalk district, being principally accumulated in thick irregular and local masses on the sides and flanks of the valleys. This is especially the case for some distance both above and below Amiens, as well as up the greater number of the lateral valleys. It extends to various elevations. A bed of gravel also spreads over some of the lower hills flanking the valley of the Somme. For full particulars of the geology of the district, I beg, however, to refer to the works before quoted of M. Buteux and Dr. Ravin.

The fall of the Somme valley‡ is very gradual, its elevation at Abbeville above the level of mean tide of the sea at St. Valery being 18 feet, at Amiens 60 feet. Between these towns the mean width of the valley, which varies but little, is rather less than a mile. The hills rise gradually to heights generally of from 200 to 400 feet, and nowhere

* Mr. Evans also has given (June 1859) to the Society of Antiquaries, an account of our visit to Abbeville and Amiens, discussing the subject from an antiquarian point of view. His paper is in course of publication in the 'Archæologia,' vol. xxxviii.

† The silt and peat in the valley of the Somme varies in thickness from 10 to 30, or even nearly 40 feet.

‡ The mean level of the river is about 8 feet below that of the valley at Abbeville.

exceed 600 to 650 feet above the sea-level, and that more in the interior of the department*. The pits in which the flint-implements have hitherto been observed are all in or near the main valley of the Somme (Map, Plate X.).

Abbeville.—According to M. Boucher de Perthes, the principal localities where flint-implements have been found are—the village of Menchecourt, a suburb at the foot of the hill on the N.W. side of Abbeville,—the town of Abbeville,—the rising ground on the S.E. side of the town on which is situated the Champ de Mars, the Moulin Quignon, and the suburb of St. Gilles—and Mautort† on the W. (Plan A, Plate X.).

Menchecourt has been long celebrated for its mammalian remains, of which a large collection was made by M. Baillon. Many of these specimens were examined and described by Cuvier‡. The chalk hills rise immediately above the village to the height of 214 feet. They are capped to the depth of a few feet by drift loam and clays: the upper part of their slope is bare, and the lower part is covered by the deposit we have to describe, and this passes under the recent peat and silt deposits of the valley. One of the largest of the Menchecourt pits is that of M. Dufour, towards the further end of the village, and on the right hand side in proceeding from Abbeville. An extensive section of the upper beds is here exhibited. The lower beds (those below *level of ground* in figs. 1, 2), of which *d* is worked during the winter, I had opened out by trenches. The one in fig. 2, which afforded the evidence of most interest, was excavated near the entrance of the pit where the upper beds are thin. The variation in the thickness of the strata is shown by another section I took at M. Deliquiere's pit (fig. 1), situated on about the same level, and at the further end of the village.

* The heights of the hills on the small outline Map in Plate X., are taken from the admirable maps of the "Département de la Guerre;" I have, however, changed the datum-line from the level of mean tide at Havre to the same level at St. Valery at the mouth of the Somme, which is 7 feet higher, and reduced the heights to English feet. I have adopted the same datum-line in the plans and sections.

† It is only lately that I have had the opportunity of visiting this locality, which is 1½ mile W. of Abbeville, and on the opposite side of the Somme. There are two pits at Mautort where flint-implements have been found, one, a shallow one, no longer worked, in the valley near the church, and another one on the side of the hill on the road leading to Moyenville, and at a height probably about equal to that of Moulin Quignon, or about 90 feet above the valley. The section, which was badly exposed on the two occasions when I was there, consists probably of—

	ft.
1. Brown sandy clay and a few angular fragments of flint	6
2. Sub-angular ochreous and ferruginous flint-gravel	4
3. White and yellow sand, irregular	3
4. Coarse light sandy, chalky, and marly flint gravel;—no bones: flint-implements said to be met with at a depth of 6 to 8 feet;—reposing upon an irregular surface of chalk	12?

The flint-implements here are remarkable for their bright white colour. The bed of gravel ceases at this elevation, but the hill rises to a height of 252 feet, showing chalk with a slight covering of red clay and flints. I also visited Drucat and St. Riquier. Near the former place there is a bed 30 feet thick of sand and gravel, but we could hear of no flint-implements or fossil bones. Nor were we more successful at St. Riquier, but our visit there was too short. (See Antiq. Celt. et Antéd. vol. ii. p. 118 to 122.)—Sept. 1860.

‡ Recherches sur les Ossemens Fossiles, edit. of 1821, vol. i. p. 110; vol. ii. p. 50, 111; vol. iv. p. 96.

*Sections in the pits at Menchecourt near Abbeville**.

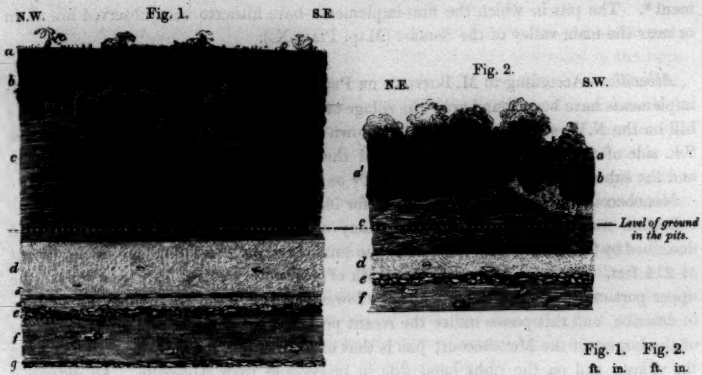

	Fig. 1. ft.	in.	Fig. 2. ft.	in.
a. Surface soil,—(and made ground, *a'*)	0	8	1	0
b. Brown clay mixed with siliceous sand, in which is imbedded a greater or lesser number of fragments of flints, mostly sharply angular, and weathered white. It is unstratified and very irregular in structure and thickness, its base forming a very indented line on *c*. It follows the slope of the ground. At places (more usually towards the base) it is mixed up with a mass of chalk rubble and flints, *b'*: sometimes the two form more distinct beds, *b* always being the upper one.	4	10	4	0
c. Light buff-coloured, fine and uniform loam (loess), with a few very thin seams and patches of small gravel, flint fragments, and of chalk grit and rubble. Very calcareous; a few small calcareous concretions. Bedding just apparent (*Sable à plaquer* of the workmen). Base wavy. *Land-shells*, *bones*, and *flint-implements*	15	0	6	0
d. Fine white sharp siliceous sand, with fine chalk débris and a few scattered large sub-angular flints and subordinate beds of light-coloured clay or marl, *d'*. (*Sable aigre*.) *Freshwater shells* often numerous and perfect, but very fragile; some *marine shells*; *bones* common, chiefly on the gravel at base: *flint-implements*	7	0	2	0
e. White and ochreous sub-angular flint-gravel and large flints but little worn, with some tertiary flint-pebbles, and chalk pebbles†, in sand same as *d*; *shells* and *bones* as in *d*, but with a larger proportion of *marine shells*, (also worked flints ?), are found in the interstices between the flints	0	8	1	0
f. Light-coloured very fine sandy marl, with a few large unworn flints here and there; in places it is indurated and very hard. (*Sable gras*.) *Shells*, chiefly land species	4	6	3	0
	32	8	17	0
g. Ochreous sub-angular gravel, just reached in section No. 1:—stopped by water.				

The ground, in M. Dufour's pit, which is on the level of the village road, is 24 feet above the highest tides of the Somme at Abbeville and 42 feet above the mean level of the sea at St. Valery.

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* All the woodcut sections are on one vertical scale, viz. 1 inch =12 feet.

† I found also two very small sub-angular and rolled fragments of some old crystalline rocks.

The gravelly clay *b* becomes more persistent and thicker as it slopes down into the valley. The loam *c*, on the contrary, is cut off gradually by *b*, and thins out: its maximum thickness is from 25 to 28 feet. The sand *d* varies from 2 to 8 feet, and is thickest about the middle of the pit. The gravel *e* is of a nearly uniform thickness of ½ to 1 foot; it apparently does not range up to the chalk, which, at the end of M. Dufour's pit, has been met with directly under the sand *d*. Of the marl *f* I examined but few sections, as the diggings do not go deeper than *e*: it appears to be rather local. The gravel *g* was reached only in the trench opened in pit fig. 1. On the opposite side of the road to pit fig. 2, a well was dug through 25 feet of gravel and sand, but no exact particulars of it were kept. A few yards beyond this the gravel passes under the great mass of silt and peat filling the valley of the Somme. In the other direction (*i. e.* up the hill) the chalk comes to the surface at the distance of a few yards beyond and above the pits; but whether it forms a cliff against which the pleistocene beds abut, or whether it passes by a rapid slope under them, there is no evidence to show.

I have given a general theoretical section of the Menchecourt deposit across M. Dufour's pit*, showing its relation to the valley and to the later deposits, in Section 1, Plate X. (See also Appendix G.)

Organic Remains.—None have been found in the upper clay and rubble, *b*, *b'*; nor could I find or hear of any worked flints having ever been met with in them.

The loam *c* contains a few mammalian remains†. The only specimens, however, that I have collected, or at present know of, are the teeth of Horse and bones of ruminants and of Elephant, all much decomposed. Some flint-implements are recorded from this bed. I found in it shells belonging to the few following land species:—

Clausilia nigricans, Mat.?	*Helix hispida*, Linn.
Helix arbustorum, Linn.?	*Pupa muscorum*, Linn.

Of these the *Helix* and *Pupa* are common, and the *Clausilia* very rare. For a list of the extraneous microscopic fossils of this and the other beds, see Appendix (E).

It is, however, to the sands and gravels *d* and *e*, which may be considered as one bed, that the greatest interest attaches, on account of the flint-implements which are found in them, and of the abundance of mammalian remains, with land, freshwater, and marine shells. The bones mostly occur in or on the seam of flint-gravel, *e*: they are often entire, but the bulk are in fragments. The land and freshwater shells are most abundant in the sand *d*; while the marine shells are more common in the gravel *e*, although a few are scattered through *d*. The following list of organic remains is taken from the

* See also the section and description of this pit in Antiq. Celt. et Antéd. vol. i. p. 232–5.

† In the accounts hitherto published of the organic remains from Menchecourt, no mention is made of those from this bed, or rather no distinction is made between those which come out of this bed and those from the strata beneath it. It is possible that some of the mammalia enumerated from *d* and *e* may also have been found in *c*, or may even be peculiar to one or the other, although there is no doubt that the great majority of the specimens are from these lower beds.

works of M. Ravin and M. Buteux, with the exception of a few additional species of Mollusca[a] marked with an asterisk.

Mammalia.

Bos primigenius, Boj.
Cervus Somonensis, Cuv.
—— *tarandus priscus*, Cuv.
Elephas primigenius, Blum.
Equus (*E. fossilis*, Owen).
Felis (*F. spelæa*, Owen).
Hyæna spelæa, Cuv.
Rhinoceros tichorhinus, Cuv.
Ursus spelæus, Blum.

Testacea.

Land.

Cyclostoma elegans, Drap.
Helix arbustorum, Drap.
—— *carthusiana*, Drap. (*H. cantiana*, Mont.)
—— *cristallina*, Drap. (*Zonites*, Müll.)
—— *hispida*, Drap.
—— *nemoralis*, Drap.
—— *pulchella*, Drap.
—— *rotundata*, Drap.
—— *striata*, Drap. (*H. caperata*, Mont.)
Pupa marginata, Drap. (*P. muscorum*, Linn.)
Succinea amphibia, Drap. (*S. putris*, Linn.)
*—— *oblonga*, Drap.
**Zua lubrica*, Müll.

Freshwater.

Cyclas palustris, Drap. (*Pisidium amnicum*, Müll.)
—— *cornea*, Linn.
**Cyrena consobrina*, Caill.
Limnæa auricularia, Mich.
—— *minuta*, Lam. (*Limneus truncatulus*, Müll.)
—— *ovata*, Drap. (*L. pereger*, Müll.)
—— *palustris*, Drap.
—— *peregra*, Drap.
—— *stagnalis*, Lam.
Planorbis marginatus, Drap.
—— *carinatus*, Drap.
*—— *corneus*, Linn.
*—— *albus*, Müll.
*—— *vortex*, Linn.
Paludina impura, Lam. (*Bithinia tentaculata*, Linn.)
Valvata piscinalis, Lam.
—— *planorbis*, Drap. (*V. cristata*, Müll.)

Marine.

Cardium edule, Lam.
**Ostrea* (one fragment).
Tellina solidula, Lam.
Buccinum undatum, Lam.
**Fusus*? (one imperfect specimen).
**Littorina littorea*, Linn.
**Nassa reticulata*, Linn.
Purpura lapillus, Lam.

I cannot say positively whether the single specimen of *Cyrena*, which is perfectly well characterized and marked by its striated teeth, came out of the gravel *e* or the sand *d*. I however picked it up myself, though it was thrown by the men out of the trench of which I was superintending the opening. A tooth of *Arvicola*, a small fish tooth, and opercula of *Bithinia*, were found under the same circumstances. Also an unperforated *Coscinopora globularis*, and a *Marginulina*, from the Chalk. On some of the flints in *e* are serpula-like markings.

The search for flint-implements was not so successful as I could have wished. As the

[a] In this list of Mollusca I have retained the original names of M. Casimir Picard (Ravin, *op. cit.* p. 199). In the other lists I have given the names adopted by Forbes and Hanley; here I have only introduced the latter as synonyms. In the Mammalia I follow generally the last lists of M. Buteux.

men were digging the gravel (*e*, fig. 2) I saw them find, enveloped in the sandy matrix (a portion of which was agglutinated on the specimens), three thin sharp-edged flint-flakes, 3 to 6 inches long. They were pronounced by M. DE PERTHES to be flint-knives, and they certainly differ from ordinary flint splinters or flakes, in that, in each case, the obtuse angle is truncated, as though to flatten the fragment and remove an unnecessary edge*. Although I cannot accept such specimens as sufficient proof, and it would have been satisfactory to have found some of the so-called flint hatchets *in situ*, I feel there is, without that direct evidence, enough moral and collateral testimony to form an opinion on the subject of M. DE PERTHES' views, supported especially as the case is by the occurrence of flint-implements elsewhere in the neighbourhood of Abbeville, and by the subsequent more easily verified discoveries at Amiens.

According to M. BOUCHER DE PERTHES, confirmed by the statements of the men, the flint-implements (*Haches*) are most commonly in the lower part of the sand *d* and in the gravel *e*.

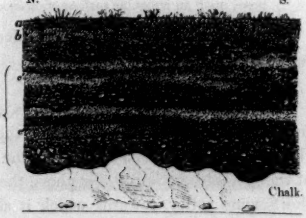
In the underlying marl, *f*, I found the few following shells, together with traces of plants (*Chara* stems?) and one very minute bone, but no flint-implements.

Cyclas?	*Limneus peregeri*, Müll.	*Trochus*? (very young).
Helix hispida, Linn.	*Planorbis albus*, Müll.	*Valvata piscinalis*, Lam.
—— *nemoralis*, Drap.	*Pupa*.	*Zua*?
—— *pulchella*, Müll.	*Rissoa*?	

Returning back through Abbeville, and ascending the gently sloping ground on the east of the town, Moulin Quignon is shortly reached, where, at a height of 106 feet above the mean level of the sea at St. Valery, is a bed of gravel showing this section.

Gravel pit adjoining the Moulin Quignon, near Abbeville.

Fig. 3.



	ft.
a. Surface soil	1
b. Brown sandy clay, gravel, and sharp flint fragments (partly removed)	2
c. Yellow, ochreous, and ferruginous gravel of sub-angular fragments of flints, and of flints but little broken—some of large size, a few Tertiary flint-pebbles, and some small sub-angular blocks of Tertiary sandstone (one, however, 2 feet long); the whole in a matrix of clay and siliceous sand of like colours, or greenish (*c''*), occasionally forming thin irregular beds by itself (*c'*). *No shells*; some *flint-implements*; a few *bones* of ruminants and teeth of *Elephas primigenius*	8 to 12 feet.

* A further examination of these specimens shows them to be so closely similar to such implements found in barrows and in peat beds, in association with admitted human works, that I am now disposed to believe in their artificial make (see fig. 7, Plate XIV.). The flint-workers of Suffolk produce this form of flint-flakes by a single sharp blow applied in a particular way to a lump of flint. A flake is thereby knocked off, which at the end which receives the blow shows a conchoidal protuberance at one side of the flat inner surface; while the outer side presents two slightly inclined planes, with their obtuse angle replaced by a small facet. This is precisely the case in these fossil flakes. Such flakes always present, as mentioned by the learned author of the Descriptive Catalogue (p. 7), with reference to the flint-knives, cutters, or scrapers in the

There is a pit of similar gravel at St. Gilles, on ground 17 feet lower and distant about half a mile to the southward. At neither of these pits did we ourselves find any flint-implements, nor had the men any; but here again they affirmed they often found them, chiefly in the lower and middle part of the undisturbed gravel, together with large bones.

Between the Moulin Quignon and the walls of Abbeville, there were formerly some gravel pits, in which a large number of worked flints were discovered; but the pits are now levelled, and the ground occupied as a "Champ de Mars." The town itself in part stands upon a bed of drift gravel and sand. In some excavations (now closed) between the Hospital and the ramparts, M. Boucher de Perthes also found remains of the Mammoth together with several flint-implements* (*ante*, p. 279).

I examined one deep excavation (fig. 4) now in progress on the N.W. side of the town. It exhibits thick beds of gravel spread out horizontally, with some interstratified seams of loam and sand, in which latter I found a few fragments of land and freshwater shells. The level of the ground here is rather lower than at the adjacent Menchecourt pits (see Sect. 2, Plate X.).

Section in the moat outside the town walls at the Porte Mercadé, 1859.

	ft.	in.
a'. Made ground	6	0
b. Angular flint-gravel in brown and ochreous sandy clay (corresponds with *b* of figs. 1 and 2)	5	0
c. Loam (loess), with thin seams of grit and gravel	6	6
d. Light-coloured sand and patches of gravel; fragments of shells (*Limneus* and *Helix*)	1	8
e. Sub-angular ochreous and white flint-gravel. Teeth of *Elephas primigenius* (one milk tooth). Reposes upon an irregular surface of chalk	2 to 4	0

Fig. 4.

Several flint-implements, generally deeply stained, have been found here†.

Amiens.—On the verge of the hills, and at a distance of three-fourths of a mile S.E. from the railway station, are situated the very interesting and extensive pits of St. Acheul (Plan B, Plate X.). According to the measurements of M. Pinsard, the mean height of the ground here is 149 feet above the mean tide level at St. Valery, and 89 feet above the Somme valley, towards which it slightly inclines, till as it approaches the valley the ground falls by a more rapid and sudden slope, while southward it stretches with a gently undulating and gradually rising surface for many miles. The site of the pits is

* collection of the Royal Irish Academy, "more or less of an obtusely triangular figure in its section." In all respect the specimens he describes and those I have seen in the British Museum, agree with the Abbeville specimens. M. de Perthes has a number of similar specimens from the pits at Menchecourt (fig. 3, Plate XII.), Moulin Quignon, and Mautort, and Dr. Rigollot figures one from St. Acheul.—September 1860.

* See Antiq. Celt. et Antéd. vol. i. p. 247 to 264, for particulars and careful sections of these excavations.

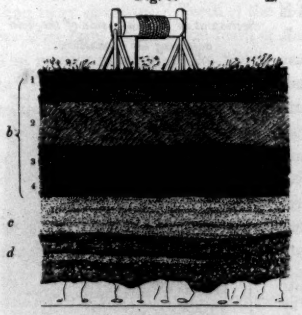
† When last there, a broken specimen, now in my possession, was discovered in the lower part of *c*, within a few inches of the gravel *e*, the sand *d* being, at that spot, almost wanting.—July 1860.

not, however, commanded by any immediate high ground, but, on the contrary, possesses an open and unobstructed view for some distance around, and is then separated, by a slight depression, from the higher hills to the southward. The pits are of considerable extent, and have been long worked for brick-earth, sand, and gravel. The total thickness of all the beds, which repose upon a very irregular and eroded surface of chalk, varies from about 20 to 30 feet. The worked flints are found chiefly in the lower bed of gravel, more particularly in the lower part of it or near the chalk, where also the greater number of bones are found, but this is by no means a general rule. A considerable number of teeth and bones are also met with in the sand and marl above the gravel.

The upper brick-earth (b^1 and b^3) has been very generally removed, so that it is only in a few places that the entire series of beds is seen, as for example, by the well in T. Freville's pit (fig. 5), near the Cagny road, at which spot they are not only more complete but more regular than usual. Further on in the same pit (fig. 6) the brick-earth has been removed, and the lower beds are more irregular. At Warean's pit, at the further extremity of the field, is another section complete from the surface to the chalk (fig. 7). These three sections show the variations in the structure of the lower beds (*c* and *d*). In conjunction with figs. 10 and 11 (p. 299), they likewise well exhibit the variations in the beds, *b**.

Sections in the pits at St. Acheul: side nearest the Cagny road.

W. Fig. 5. E.



W. Fig. 6 E.

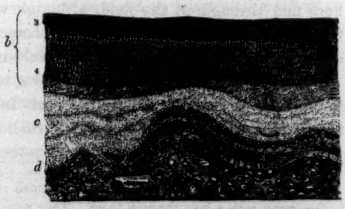


		Fig 5. ft.	Fig 5. in.	Fig. 6. ft.	Fig. 6. in.
a.	Surface soil	0	8	removed for brick-earth.	
b. 1.	Brown loam, slightly calcareous, with a few sharp flint fragments	2	10		
2.	Ditto lighter coloured, finer, and more calcareous	5	0		
3.	Ditto darker; not calcareous, and mixed with more or fewer angular fragments of flints, passing in places into a complete gravel	2	0	1	6
4.	Ditto coarser and darker; in places calcareous; traces of carbonaceous matter	2	4	4	2

* *No organic remains have been found in the above beds.*

* See also the sections and ground plan of the pit by Dr. Rigollot, *op. cit.* pp. 33–36, pl. 3–5.

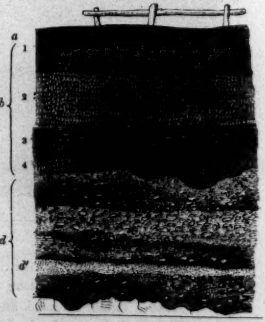
	Fig. 5. ft.	in.	Fig. 6 ft.	in.
c. White siliceous sand and light-coloured marl, mixed with fine chalk grit; a few large sub-angular flints, and an occasional sandstone block; irregular patches of flint-gravel; bedding waved and contorted; here and there layers with diagonal seams; a few ochreous bands; portions concreted. *Land* and *freshwater shells* common; some *mammalian remains*; (*flint-implements*?)	4	10	7	4
d. Coarse sub-angular flint-gravel in a base of white siliceous sand with chalk grit; occasionally coloured ochreous and ferruginous in irregular layers; a few black layers. Some large and whole flints, and some fragments angular, especially many small ones. Much fine chalk débris, pebbles, and small blocks rolled but not rounded. Numerous sub-angular pieces and blocks, small and large, of Tertiary (lower Eocene) sandstone; Tertiary flint-pebbles abundant; occasional specimens of Tertiary pudding-stone, and a few chalk (*Inoceramus*, *Pecten*, *Belemnites*, *Echini*, *Foraminifera*, &c.) and Tertiary fossils (*Venericardia planicosta*, *Nummulites* and other *Foraminifera*), are dispersed through this gravel. Subordinate seams of sand. Bedding in places level and in other places contorted, especially the upper surface. *Mammalian remains* and *flint-implements* dispersed throughout, but chiefly in the lower part. *Shells*, mostly in fragments (*Helix*, *Limneus*, *Pisidium*, *Pupa*), in some of the seams of interstratified sand*	5	0	6	0
	22	8	19	

The blocks of sandstone are very numerous and large, especially in the pits nearest the high road, some measuring as much as 3 to 4 feet in length, and weighing ½ to 1 ton†.

In the east of the field the sand *c* thins out, and is replaced by the gravel *d*‡, as shown in section fig. 7, where a good many remains of the Elephant have been found, and but few flint-implements. The beds here and throughout the field, although varying in thickness, have the same general composition as described in figs. 5 and 6. (*d'* is a local sand seam.)

Section at St. Acheul: side of the field adjoining the Monastery.

N.W. Fig. 7. S.E.



One chief object in visiting the pits was to discover for myself, if possible, flint-implements *in situ*, or, failing in that, to be able to certify to their discovery

* In this gravel there are also found some small round white bodies, many with a hole through them. They were noticed by Dr. Rigollot (*op. cit.* p. 16), who suggested that they might be beads made of hard chalk. They are not rare. I doubt, however, their being in any way artificial, for their globular form is natural, they being a common chalk fossil, the *Coscinopora globularis*, D'Orb. This is a small globular sponge or foraminifer, of which the top is often more or less open or perforated. They are abundant on many parts of our chalk coast, especially at Newhaven, where I have found them on the shore, some whole and some perforated, precisely like those in the gravel of St. Acheul (now the *Orbitolina concava* of Parker and Jones, 1860).

† There was one found which, judging from the number of door-steps (about 18) and paving stones (about 100) it furnished, must have weighed 4 or 5 tons.

‡ In one pit, nearly in the centre of the field, the sand was 16 feet thick, and the gravel almost wanting.

by the workmen. The long fresh faces of gravel afford, together with the digging for gravel in daily operation, ready and convenient sections for observation. On my first visit, notwithstanding a careful personal search, I found neither bones nor worked flints. I, however, obtained a number of the latter from the men, some of which were dug out whilst I was there; and in the overlying sand I found numerous land and freshwater shells, consisting of the following species:—

Cyclas cornea, Linn.	*Limneus palustris*, Linn.	*Pupa muscorum*, Linn.
Pisidium amnicum, Müll.	—— *pereger*, Müll.	*Succinea putris*, Linn.
Ancylus fluviatilis, Müll.?	—— *truncatulus*, Müll.	„ (var. *Pfeifferi*).
Bithinia tentaculata, Linn.	*Planorbis albus*, Müll.	*Valvata piscinalis*, Lam.
Helix nemoralis, Drap.	—— *marginatus*, Drap.	*Zonites radiatulus*, Ald.?
—— *hispida*, Linn.	—— *spirorbis*, Linn.	
—— *rotundata* (Buteux).	—— *vortex*, Linn.	

Remains of the following species of Mammalia have also been found at these pits:—

Bos (*primigenius*?)	*Elephas antiquus*, Falc*.	*Equus fossilis*, Owen.
Cervus.	—— *primigenius*, Blum.	

Entire bones are comparatively rare in these pits, but fragments, more or less worn, are tolerably common. A portion, however, 4 feet long, of the tusk of an Elephant was recently met with; but it is more common to find it in small pieces, easily recognized by their ivory structure. Teeth of the Horse in a perfect and unimpaired condition are also far from rare, whilst entire teeth of the *Elephas primigenius* are not unfrequently found. The greater number of the bones are soft, light, and friable, and without any addition to their own earthy constituents; and having lost their animal matter, they mostly adhere strongly to the tongue. Some, however, have received an additional portion of carbonate of lime, whereby their weight is considerably increased. The enamel of the teeth is generally but little changed. Some of the fossils are more or less bleached; others are coloured by the peroxide of iron present in some layers of the gravel.

I had, however, hardly reached Abbeville when I received a telegraphic message from M. Pinsard, to inform me that a worked flint had been discovered *in situ*, and left for my inspection. I immediately returned, accompanied this time by Mr. Evans†. As this was, I believe, the first flint-implement examined *in situ* at these pits by any geologists, I feel it necessary to describe it at some length. It was lying flat in the gravel, at a depth of 17 feet from the original surface‡, and 6½ feet from the chalk. One side slightly projected. The gravel around was undisturbed, and presented its usual perpendicular face. I carefully examined the specimen, and saw no reason to doubt

* Dr. Falconer has just informed me of his determination of this species, and of some other interesting facts connected with the fossil bones at Amiens. I have, with his permission, given an extract of his letter in the Appendix (B).—November 1860.

† M. Pinsard was also present, together with MM. Dufour and Garnier, the President and Secretary of the "Société des Antiquaires de Picardie."

‡ Six feet of the brick-earth at top had been removed. The bottom of the pit was 2 feet above the chalk.

that it was in its natural position, for the gravel is generally so loose, that a blow with a pick disturbs and brings it down for some way around; and the matrix is too little adhesive to admit of its being built up again as before with the same materials. At this spot the matrix of the gravel consisted of the usual chalky sand; the seam was continuous, the fragments of flint were in their ordinary position, and the cohesion of them and of the worked flint in the face of the gravel was exactly of the same strength. I found also afterwards, on taking out the flint, that it was the thinnest side which projected, the other side being less finished and much thicker,—a position therefore the reverse of that which would have been adopted had it been pushed in; if it had been, the hole made by the ingress of the thicker edge would have left the projecting thinner edge unsecured, whereas the matrix was close up to it all around, and neither harder, looser, nor differing in texture or colour from the adjacent portion of the gravel. When also I removed this implement *, I found that the sand, in all its minute indentations, corresponded exactly with the matrix of that particular seam of the gravel. I carefully examined the ground above, and could detect no trace of any artificial disturbance. Each bed followed its natural course above the place where the flint-implement was imbedded, and the lines of division of the upper brown gravel and clay, of the light-coloured sands, and of the lower gravel, were continuous and unbroken. The section at this spot was as under—

		feet.
b.	Brick-earth (removed)	6
	Brown sandy clay and gravel	1½
	Brown sandy clay, reposing upon an irregular surface of *c*	2½
c.	While chalky sand with freshwater shells, thinning out at one end of the section	3
d.	Coarse gravel, in which, at a depth of 4 feet, the *flint-implement* was imbedded	8½

In another and deeper part of the pit, the workmen on the same day turned out, amongst the dug gravel, two more perfect specimens of flint-implements, from depths respectively of 20 and 24 feet beneath the original surface. Portions of the white calcareous matrix still adhered to these implements, and they were partly stained ochreous, like one portion of the gravel with which they were in contact. This part of the pit was, like the other, perfectly undisturbed. The bed of sand over the gravel was, however, more developed and more argillaceous, and I found in it, immediately above the place where the flints were lying, many perfect specimens of the fragile *Limneus*, *Succinea*, *Planorbis*, and *Helix*. The workmen brought us some ten or twelve more flint-implements recently discovered. They all affirmed these flints† to be found low down in the gravel and in unbroken ground (*terrain vierge*). When the pits are in full work, a day rarely passes without some of these objects being met with. The number is in fact one

* This implement is rougher and more imperfect than the generality of the specimens; still it exhibits evident traces of working, especially on one side and at the point. It is an unfinished implement, resembling in that respect several I have since seen.

† Now commonly known to them by the name of "Haches." The children sometimes call them "Langues de Chat." I may observe that our visit, both at Abbeville and Amiens, was entirely unforeseen and unexpected, and very little value was then placed on either flint-implements or fossils.

of the surprising features of the case. Dr. RIGOLLOT mentions that between August and December 1854, above 400 of such specimens were found at St. Acheul, and that, from the time he began collecting, 150 had been brought to him*. They are not found together or in heaps, but separately and at greater or less intervals. The bulk of them show very little appearance of wear. Many are as sharp and fresh-looking as though they had but recently come from the hands of the workman. I have, however, some which are distinctly worn; and a few specimens which had been broken before they were entombed, as shown by the colour and staining of the fractured surface, in particular exhibit a blunting of the broken edges. Some are unfinished, and some retain portions of the outer original chalky crust, wherever it suited the form of the implement. They are said by Dr. RIGOLLOT never to be found either in the upper brown clay or gravel, *b* †.

We afterwards visited several neighbouring gravel pits, with a view to determine the relation which the beds at St. Acheul bore to the other drift beds of the district. At St. Roch, on the south-west of Amiens, and 1¼ mile distant from St. Acheul, is a large gravel pit, celebrated for the number of its mammalian remains‡. It is situated on the lower part of the hill, sloping down to the valley. The gravel consists, like that at St. Acheul,—except that it has fewer ferruginous or ochreous seams and sandstone blocks, and more chalk débris,—of a mass of loosely packed white and light-coloured sub-angular flints, tertiary flint-pebbles and sandstones, sand, and chalk rubble, from 20 to 28 feet deep, overlaid by 3 to 8 feet of brick-earth. The following is the list of mammalian remains from this locality:—

Bos primigenius, Boj. *Elephas primigenius*, Blum. *Hippopotamus* §.
Cervus somonensis, Cuv. *Equus* (*E. fossilis*, Owen). *Rhinoceros tichorhinus*, Cuv.
Elephas antiquus, Falc.

We found no shells in any part of this pit. Dr. RIGOLLOT states that some few flint-implements have been met with; but we discovered none, nor could we hear of any having been recently found. The level of the ground is lower than that at St. Acheul, extending from about 45 to 60 feet above the Somme; and the gravel does not range up the hill, but abuts against it, and is commanded by the chalk hills, as the sand at

* *Op. cit.* p. 15. On my first visit we brought away from the pits about 26 specimens; on a second visit 38; on a third visit 32; and on a fourth visit 14. It must not, however, be supposed that they are easily found. They require a long and careful search.

† I have since had reason to question this point, but the evidence is contradictory.

‡ There is a collection of the fossil bones from this pit in the Museum at the Botanic Garden. They are mostly more blanched and decomposed than those at St. Acheul, and are generally very friable, though many of the specimens are perfect in shape and well preserved. Teeth of the *Elephas primigenius* and of the *Rhinoceros tichorhinus* are common. See BUTEUX, *op. cit.* p. 71, and RIGOLLOT, *op. cit.* p. 35.

§ On my second visit to this pit we obtained from one of the workmen four fine and well-preserved tusk teeth of the *Hippopotamus*,—a genus not previously noted from this place. The *Elephas antiquus* has also just been noted by Dr. FALCONER.—November 1860.

Menchecourt. In proceeding to St. Acheul, at a short distance eastward, and nearly on the same level, is a bed of 15 to 20 feet of clay and sand. A little way higher up the hill the chalk comes to the surface, or is merely covered by 2 or 3 feet of brick-earth. The beds at St. Roch and St. Acheul, whatever may have been the case originally, are not now continuous. Still they trend one towards the other round the base of the hill, having been traced along part of the railway cutting.

Note.—I again visited Abbeville and Amiens in June 1859 with some other Members of the Geological Society. On this occasion my friend Mr. J. W. Flower succeeded, after some search, in disinterring *with his own hands* a fine and large flint-implement at a depth of 22 feet from the original surface of the ground,—an important and conclusive fact to which we all bore witness. An account of this discovery has been communicated to the Geological Society. (Quart. Journ. vol. xvi. p. 190.)

Shortly afterwards Sir Charles Lyell visited the pits, and expressed an opinion confirmative of the antiquity of the flints at the Meeting of the British Association at Aberdeen (see Report of the Proceedings). He was followed by M. Gaudry of Paris, who spent several days at Amiens for the purpose of exploring the pits, and witnessed the finding of nine flint-implements. The result of his observations he communicated to the Institute of France in October 1859 (see the Comptes Rendus of the 3rd Oct.). M. George Pouchet, of Rouen, deputed by the municipality of Rouen to visit the pits, published a report, in which he described his having seen and extracted a worked flint *in situ*, and fully confirming M. Boucher de Perthes' discovery (Actes du Mus. d'Hist. Nat. de Rouen, 1860, p. 33). M. Desnoyers and M. Hébert have also made a further examination of this singular locality, respecting which M. Hébert has given some additional explanation to the Geological Society of France (Bull. vol. xvii. p. 103).—April 1860.

§ 3. NATURE AND VALUE OF THE EVIDENCE.

Questions have been raised,—1st, as to whether the so-called flint-implements have really been fashioned by the hand of man; 2ndly, whether they can be of recent manufacture; 3rdly, whether they could have got into their present position subsequently to the formation of the beds in which they are found, or whether they truly belong to the same period.

1 Under ordinary circumstances I should hardly have deemed it necessary to touch, in a geological paper, upon some of the following points, if satisfied myself with the evidence usually deemed conclusive in like cases. In a question, however, of this importance, a few remarks, which to many will, I fear, appear supererogatory, seem required to meet the various objections that have been raised.

It is essential, as a preliminary step, to recollect that the argument does not rest upon the evidence of skill, but upon the evidence of design. The skill being rude (for the flints are only chipped into form and in no degree ground down) is not always evident at first sight, and hence the existence of design has been sometimes denied. Flints from the chalk hills of the district itself readily supplied the material of which the flint-implements are formed. The exterior of all chalk flints invariably presents a white earthy crust, from which small fossils frequently project, while the interior of the flint is black or dusky, but clear and semi-transparent. The fracture is conchoidal or splintery; and there is no tendency to break in one direction rather than in

another*. It may happen that a shattered flint (by whatever natural cause produced) should give flakes or splinters closely resembling simple forms produced by one or two blows applied artificially. But here the coincidence must cease; for it is obvious that blows applied by hazard and resulting from natural causes, as in a *mêlée* of gravel, would necessarily multiply their direction of strike in proportion as the blows themselves were multiplied, and consequently the shape of the flint would tend, up to a certain point, to become more and more irregular; whereas, on the contrary, blows applied by design, and with a given object in view, would tend to give to the flint more and more finish, form, and evident art. So with respect to the flints in the gravel the more broken the more irregular, whereas, on the contrary, with the flint-implements the more they are chipped and broken the clearer is the design. In many lance-head shaped specimens both sides show two plane surfaces meeting at an obtuse angle, each plane formed by ten to twelve parallel chips, and in these and all cases every blow or chip has distinct reference to the ulterior form (see figs. 5 and 8, Plates XIII. & XIV.).

With regard to the possibility of the flint-implements resulting from natural wear, I have already mentioned that in many of the specimens the outer coat of the flint is frequently adapted and left, when possible or convenient, in the finished instrument (see fig. 4, Plate XIII.), and such original surfaces show so little trace of wear that small delicate fossils, so often found projecting on them, still remain untouched. If the flint had been so extensively fashioned by wear, how could one portion, and always a prominent part, have remained unworn, while other portions have been so largely abraded†? Besides, the tendency of wear, if sufficiently long continued, is ultimately to reduce the flints to the rounded form of pebbles, a condition of things incompatible with the retention of the sharp points and cutting edges of these implements.

But it is not so much upon the improbability of the chances of natural causes producing such forms, as upon the unity of character and evident object in the design, that the argument of artificial make is the strongest. Even if some natural cause did tend to produce deceptive forms, it would be, as before mentioned, according to some one given simple type, such as the flint knives or single flakes; but in these implements we find three principal types‡,—one, lance-shaped (fig. 8); a second, almond-shaped (fig. 5); and a third smaller form, a flattened ovoid (fig. 1), (Plate XII. to XIV.). In length they vary from 2 to 11 inches, a medium size being the most general. These forms are constant, and each type presents a nearly constant relation between the length and breadth of the specimens. In A there is a sharp point, with a central, and often high, midrib on either side; in B we find a rounded cutting end, the sides flatter, and the midrib is less marked. In both forms one end is generally large and blunt, and the side-edges sharp; and advantage is taken, at the blunt end, of the original outer surface and form

* Or as the gun-flint makers observe, "flint has no grain." It has not in fact the slightest cleavage.

† Where they have undergone wear in the gravel, they, like the ordinary flints, have their edges blunted and are irregularly broken, and they are not unfrequently truncated at the point.

‡ Besides some minor ones, as flint-flakes, and the leaf-shaped implements of Mautort (figs. 2,3, Plate XII.).

of the flint. In C the whole flint is worked; the cutting edge extends all round, and the midrib is not so distinct, or is rounded off. Now, it is to be observed that these cutting edges are always on one plane, and that they were produced by blows applied at the edge—the occasional splintering caused by the blow being generally apparent;—and that the sides are equilateral. This regularity of structure surely implies design, the application of forethought, and an intelligent purpose. One object is apparent throughout, that of giving to a hard durable substance a shape either sharp-pointed or cutting. Nothing surely but the human hand could have directed a series of blows not only parallel one with the other on each surface, but also carefully directed along and maintained on one given plane, and resulting in producing a symmetrical form. Under natural conditions of fracture, the greater number of blows would, on ordinary chances, fall on the broadest surfaces of these flints, and no sharp point and angle could be permanently maintained, still less gradually elaborated.

In considering this point I have confined myself to the one set of implements termed "Haches" by M. Boucher de Perthes*. On many of the other forms noticed by that gentleman there might reasonably be more difference of opinion. It suffices for our purpose, in treating of the geological question, that we have one set of implements showing art and design.

Lastly, all these flint-implements exhibit a peculiar and distinct type and a general agreement in finish and shape. They are not copied from any other form, nor do any others exactly resemble them†.

2. On the second point various considerations present themselves. If, however, the question can be settled upon the single character of the effects of weathering on the specimens our end will be attained; at the same time other objections will incidentally be disposed of. Some chalk flints when broken retain their clear dark surfaces comparatively unaltered for ages; others, on the contrary, weather white in the course of a few years‡. When, however, the flints are imbedded in gravel, the alteration depends more upon the nature of the matrix. The broken flints there retain, in some parts, their black surfaces fresh and unchanged, but with a more marked vitreous lustre than in freshly broken flint; while in other parts of the same bed they are stained more or less deeply by the nature of the matrix in which they are imbedded. Thus in siliceous and chalky sand, flints will remain unaltered; in some marls and clays they become opaque, white, and bright as porcelain; in ochreous sand, especially if argillaceous, they stain yellow, whilst in ferruginous sands and clays they assume a brown colour. This staining is so

* *Op. cit.* vol. i. p. 347–77.

† The ordinary so-called stone celt is squarer and more chisel-shaped, and is generally more or less ground. The flint flakes or knives found at Menchecourt, and one figured by Dr. Rigollot from St. Acheul, seem, however, identical with the more recent specimens. For fuller information connected with these various points, see Mr. Evans's interesting letter in Appendix (A), and his paper before referred to.

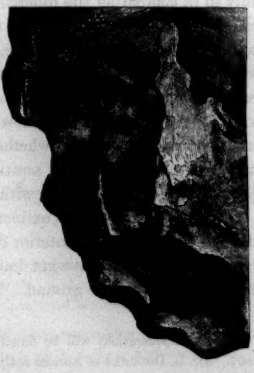
‡ In the old part (11th century) of the Tower of London and in the old Norwich and other churches, the flints still show a dark surface but little altered by long exposure.

strong and permanent, that no subsequent exposure will remove it. In studying the drift deposits, I have found it a convenient test whereby to trace one set of flints from the gravel of one period to that of another, when the general appearance of the two gravels has been so much alike, that, but for the presence of these derived portions, it would be difficult to separate them. Now in looking over M. Boucher de Perthes' fine collection, you are at once struck with the fact, that the flint-implements from each locality present a colouring in perfect accordance with the lithological character of the bed of which they had formed part, indicating, I believe, not only a real derivation from such beds, but also a sojourn therein of equal duration to that of the naturally broken flints occurring in or forming part of the same beds. Some of those from the sand *d* of Menchecourt are not discoloured; others, however, exhibit a more or less white porcelanic coating. This depends probably upon the occasional presence in the sand *d* of white clayey and marly seams (*d'*). Those from the ochreous gravel of Moulin Quignon are, on the contrary, stained of a bright yellow or ferruginous colour. The same variations exist at St. Acheul; some of the flint-implements still retaining their fresh black surfaces, whilst others are weathered white or ochreous, according to the character of the particular seam of gravel in which they are met with, the unaltered ones being the most frequent, as the white gravel is in the largest proportion.

In the next place, these flint-implements, not being ground or polished, present a rough surface, often with many small hollows and angles in which the matrix can lodge; and in all the specimens from the different localities, which still retained portions of the

Fig. 8.

Fig. 9.



matrix, either in such cavities or adhering to the surface, the material was invariably in accordance with that of the bed from which they were reported to have come.

Further, many of the worked flints, especially those at St. Acheul, are coated, more

or less, on their chipped or made surfaces, by a film of deposited carbonate of lime (fig. 8); some also are marked with superficial dendritic impressions (fig. 9),—both features only to be produced by considerable time, and both common on the flints composing the mass of the gravel itself. The preceding figures represent portions ($\frac{1}{4}$), twice enlarged, of two specimens from St. Acheul on which these characters are exhibited*.

That we may often pass a considerable time in examining a section of drift gravel known to contain mammalian bones, and yet not succeed in discovering any, must have been experienced by all who have worked at beds of this age. In such cases the specimens are necessarily obtained from the workmen, whose opportunities are constant. I have been, time after time, to the well-known pits at Grays Thurrock, which have supplied so rich a series of mammalian remains to our museums, and never found a single specimen by my own search. At Ilford and Erith I have, on the contrary, readily procured an abundance of small specimens with my own hands. Again, the large gravel pit adjoining the Croydon Station, was extensively worked for several years before the fragment of a bone was found, and then the men found only a few rare pieces of the tooth and tusk of the Elephant. When, therefore, the remains are not abundant, the evidence of their really occurring in the position assigned to them must depend, in great measure, upon the honesty and veracity of the men, and on the concordance and condition of the fossils. I have rarely, on such occasions, had cause to doubt the former, nor, after a little experience, have I had much difficulty in deciding with regard to the latter. The workmen with whom I came into contact in France seemed to me as generally equally deserving of confidence. Their testimony was given freely, and was concurrent at each locality, and equally so in comparing the different localities between which there was little or no communication. Now all the workmen to whom I spoke, both at Abbeville and Amiens, were unanimous in assuring me that the flint-implements were found in the undisturbed gravel indiscriminately with the fossil bones. Not only did the workmen all agree on this point, but the foremen and proprietors of the pits bore testimony to the same fact,—a fact which to a certain extent I can now corroborate from my own experience†.

3. Finally, we have to consider whether it is possible for the flint-implements to have been introduced into their present position within some comparatively recent period, or whether they are contemporaneous with the accumulation of the gravel; and further, whether the remains of the large extinct mammals could have been derived from some older beds, and therefore be of anterior date to the flint-implements.

These implements might have got imbedded in the gravel,—1st, by artificial excavations; 2ndly, by rents in the ground. To anybody accustomed to the examination of

* Many of these considerations will be found alluded to by M. Boucher de Perthes, as well as by Dr. Rigollot. Dr. L. Douchet of Amiens aptly observes that these incrustations "sont pour nous ce que la patine est pour la medaille.....la preuve ou le signe impossible à nier de leur antique origine" (Antiq. Celt. et Antéd. vol. ii. p. 431).

† That we have to regret attempts at, as well as successful instances of, deception, must be admitted; but that such are the exception to the general rule I am, from long experience, fully satisfied.

drift deposits, there is little difficulty in distinguishing between the fresh and uniform appearance of undisturbed beds, and the mixed and confused make of made ground, independently of the occurrence of any charred materials, pottery, &c., and of bones in a comparatively fresh condition. The lines of original stratification once broken cannot be so restored as not to show the break of continuity. In the St. Acheul pits, the several divisions of the gravelly clay, *b* (figs. 5, 6, 7, 10, 11), and the two of the underlying sands and gravel, *c*, *d*, each present distinct divisional lines and differences in colour. Now these lines and this bedding continue uninterruptedly over the portion of the lower gravel where the flint-implements are found. There is no break, no disturbance, and the small delicate fossils in the sand *c* remain uninjured, except at such places where the ground has been dug for brick-earth or otherwise excavated, and then the disturbance is sufficiently apparent. At St. Acheul part of the field was occupied for several centuries as a Gallo-Roman burying ground. But the old sepultures rarely extend deeper than the brick-earth and gravel, *b*. Some fine specimens of stone coffins (of the hard and sandy lower chalk) remain on the ground, the surrounding brick-earth having been excavated. Of the wooden coffins nothing but the ironwork remains. Roman coins, and fragments of old pottery are found on or near the surface, and the new ground is, in places, strewed with human bones. The following sections in F. FREVILLE'S pits, show how distinct the line is between the disturbed and undisturbed ground.

Sections in the pits near the high road at St. Acheul..

Fig. 10.

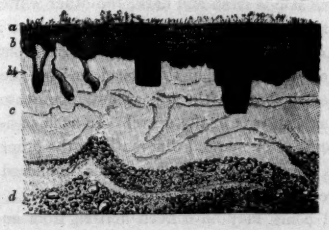


Fig. 11.

	Fig. 10. ft.	in.	Fig. 11. ft.	in.
a. Surface soil;—*a'*. Made ground and graves (7½ feet and 9½ feet) with human bones	0	6	0	6
b. Brown sandy clay and angular gravel; the lower bed (*b* 4) is almost wanting	6	0	6	6
c. Whitish sandy marl with yellow seams: few shells: contorted lamination.....	6	0	5	6

d. White gravel, irregular and contorted. For details of the composition of these beds, see description of figs. 5 and 6, pp. 289, 290. There are more bones and teeth, and fewer flint-implements, here than in the pits nearer the Cagny road.

At Menchecourt I found the ground disturbed in one spot to a depth of 6 feet, but everywhere else it was undisturbed beyond a depth of 1 to 2 feet. In no case did I

find the white sand *d* (figs. 1, 2, p. 284), in which the flint-implements are chiefly found, in any way disturbed. The depths noted on some of the specimens in M. DE PERTHES' collection, such as 4, 5, 6, and 7 mètres, sufficiently remove them from the probability of ordinary superficial disturbing causes.

Rents may have arisen from desiccation of the surface or from earthquake movements. In the former case, such gaps would necessarily be filled up from the sides or from the surface, and a vertical seam of matter, differing more or less from the beds it cut through, would be traceable from the surface down to the flint-implements, but there is not the slightest appearance of such a state of things in these pits. The same objection would apply to openings produced by earthquake movements, though to a lesser extent, as such might have closed up again and not remained open until filled up. Still, with gaps in such loose materials, and on the assumption that the flint-implements themselves fell into such gaps, other stones, dirt, and parts of the walls must inevitably have also fallen down and shown traces of the presence of materials foreign to the several beds; this is not the case. Also the fine lamination common in the bed of sand (*c*) forms continuous and unbroken lines. Besides, as irreconcileable with any contingency which would have led to the introduction of the flint-implements from the ground above, the flint-implements are dispersed singly and irregularly, are limited to the one lower series, and lie apparently flat in the gravel, and not edgeways or downwards. The specimen extracted by myself was certainly, and the one found by Mr. FLOWER was apparently, in that position. In a certain proportion of the specimens from St. Acheul, I have also observed that the two sides of the flint-implements present a different appearance, being stained and coloured differently; sometimes one side is fresh and dark, the other white and with dendritic markings; others are white on one side and brown on the other; others again have a calcareous film on one side only. These appearances may arise from the specimens having lain between differently coloured seams of the gravel, or from the percolation of water lodging on one surface more than on the other; but in no case could it have arisen had they been edgeways or endways in the gravel. In such positions one end, portion, or segment might be stained or marked differently to the other end or another portion, but the two flat sides could not possibly have been immersed each in a different medium, in the way indicated by their present condition.

The remaining question, whether the fossil bones may have been derived from an older deposit, presents a contingency requiring especial notice. That such a case is possible, is evident from the circumstance of fossils and débris of various Tertiary strata being found in the gravel. Still there are, I think, valid objections to this supposition. 1. The fragments of bones, although constantly found with their sharp angles worn and blunted, never assume a rounded pebble-form, or exhibit an extent of wear materially differing from or exceeding that to which the flint-implements themselves have been subjected; while, as a general rule, the entire bones and the teeth are either not rolled at all, or are so slightly so, as rarely to be in any way injured by attrition. If the bones were really derived from an older bed, then consequently they would

in general be worn as much as any other materials derived from such a source,—a wear necessarily in excess of that of the newer portion of the gravel,—whereas, on the contrary, the bones are amongst the least worn substances in it*. 2. Neither do the bones or teeth show any mineral character, nor is there any substance adhering to them, different to that which would be imparted by the matrix in which they are now imbedded. Nor, if they had only been originally subjected to their actual extent of mineral change, would they have been in a better condition to resist destruction by subsequent exposure and wear than they are now. The teeth of the Elephant are mostly much decomposed, and tend, without great care, to fall to pieces on exposure. Many of the bones are also very friable, the greater number being porous and free from any foreign matter. 3. No older beds, that could have furnished such mammalian remains, are known to exist in the district†. 4. The delicate and friable shells, found associated with the bones at St. Acheul and Menchecourt, and that could not possibly have withstood any transfer, are such as are associated with similar remains elsewhere in France and in England, where we have no reason to doubt the contemporaneity of the two sets of organisms. 5. At St. Acheul part of the lower jaw with the teeth, and considerable lengths (4 and 5 feet) of the tusk, of *E. primigenius* have been found. At Menchecourt the bones of the leg, lying in their natural position, and nearly the whole skeleton of a *Rhinoceros*, were found entire‡,—the first being an improbable, and the second an impossible contingency, had the remains of the animal been washed out or removed from some older deposit. 6. Lastly, the extinct mammalia are of species which occur, both in England and France, only in the latest geological deposits, whereas if these remains were here extraneous, we should expect to find some species peculiar to deposits of anterior date.

An objection has also been taken on the score of the large number of flint-implements discovered at St. Acheul. But this is confounding two distinct propositions. To substantiate the discovery of a fact, it is not necessary to be prepared with an explanation of all the phenomena connected with it. In this light it, no doubt, presents a difficulty, which, however, it is to be hoped that future research will clear up§. I may mention in

* The wear which will hardly affect a flint-fragment will reduce a calcareous stone to a pebble-form. The local gravel of an oolitic district is usually composed of smooth flat pebbles, whilst if flint-fragments are present, as is common, they are angular or subangular. Extraneous fossils, as in the Crag, necessarily present, in general, the maximum of wear, besides showing more or less lithological dissimilarity.

† It is quite possible, at the same time, that here, as elsewhere, older gravel beds may have furnished some of the materials of this gravel. In fact I should judge such to be the case, from the circumstance of many of the flints found in the white chalky beds being of a brown colour and all the edges rounded, showing therefore a mineral condition incompatible with their present position, and a large amount of wear.

‡ On this essential point I give the evidence of a late distinguished naturalist of Abbeville. Appendix (C).

§ To show, however, how abundant flint-instruments must have been at periods when the use of metals was in its infancy or unknown—at Cantin, near Douay, there were found, in 1824, 600 ancient flint flakes or knives amassed together in one heap (Mém. Soc. d'Emul. d'Abbeville for 1836–37, p. 257); and the eminent antiquary, M. Worsaae, of Copenhagen, in a letter written with reference to this subject, mentions that he and a friend "collected, in the course of a few weeks, more than a thousand rude flint-implements" on the borders and islands of the small lake of Maribo. (The Athenæum for 31 December, 1859, p. 889.) —November, 1860.

the meantime that, although these flints are so numerous in one pit at St. Acheul, they are scarcer in the other pits in the same field; that at Menchecourt they are rare, still rarer at St. Gilles, more common again at the Champ de Mars; whilst at the large gravel pits* of St. Roch, Boves, and Montiers near Amiens, where the St. Acheul discoveries were perfectly well known, and search has been frequently made, I could neither find, nor procure from the men, any flint-implements. See Appendix (D.)

§ 4. GEOLOGICAL CONSIDERATIONS.

I should not wish, until after fuller study of the district, to enter on the question regarding the mode of formation of the above-described deposits of Abbeville and Amiens, beyond pointing out, that, at the former place, the evidence of the lower beds of Menchecourt having been deposited partly in fresh water, and partly in salt or brackish water, seems sufficiently clear and distinct. Apart from the latter condition, the St. Acheul sands (*c*), as well as the lower gravel (*d*) containing the flint-implements, may also be attributed to a like accumulation under fresh water. The upper beds (*b*) in both cases are, I believe, of entirely different origin, and belong to a class of phenomena of far wider extent and generality. At the same time, while postponing the more theoretical questions, the one concerning the relative age of the deposits can, to a certain extent, be considered independently upon the evidence of the organic remains and of correlation; and certain general conclusions may be ventured upon.

It is probable that subsequently to that phase of the Glacial period marked by the Boulder Clay, the area of dry land became more extended, and on it there lived the *Elephas primigenius* and *E. antiquus*, *Rhinoceros tichorhinus*, *Hyæna spelæa*, with species of *Deer*, *Horse*, and other animals, mostly of extinct, but some of species not to be distinguished from the recent; whilst the waters of both sea and land were tenanted almost exclusively by shells of recent species still common in this and adjacent countries. The remains of this old surface we find in deposits, which everywhere contain a similar group of organic remains, and occur mostly in old valleys or at moderate elevations. They are never overlaid by other fossiliferous deposits, and I believe them all to belong to a state of things which immediately preceded the present order. One feature of these deposits is, that although closely related to the present configuration of the surface, yet they are always more or less independent of it. They are often near present lines of drainage, yet could not, as a whole, possibly have been formed under their operation. The deposits described in the preceding pages are, there is little doubt, of this age, and they have many analogues in France and England. The Menchecourt beds bear a very close resemblance (the marine characters apart) to those of Fisherton† near Salisbury‡. The deposit of St. Acheul is like, in many respects, the Ilford and the Brentford beds, whilst that of Moulin Quignon and St. Gilles closely resembles the gravel beds at Croydon, Wandsworth Common, and some other places near London.

* All on a lower level than St. Acheul, but with like mammalian remains,—showing like wear.

† Quart. Journ. Geol. Soc. vol. xi. p. 102.

‡ Also of Orton, near Peterborough, where marine remains do occur.

The gravels of Moulin Quignon and St. Acheul are placed respectively 88 and 89 feet above the valley of the Somme, are not commanded by any higher ground immediately adjacent, and are out of reach of all running water, or of any possible interference from agents in present action. At Menchecourt and St. Roch, on the contrary, the beds are placed against the side of the chalk hills, and slope from a height of about 60 feet down to the valley. Still these lower-level deposits are, although not to the same degree, quite beyond the agency of present river action, and are independent of recent changes.

It is probable that the various beds, although on these different levels, belong to the same general period, and may be nearly synchronous. Had I, however, been asked to decide upon physical evidence alone, I might have been disposed to consider the gravels on the low hills of Moulin Quignon and St. Acheul as a stage anterior to those of Menchecourt and St. Roch; but although I throw out the suggestion for the purpose of directing attention to the point, as one not to be overlooked, it is one which could not be decided without further evidence, and which I should hesitate at present to adopt. It is sufficient, for the object we have under immediate consideration, to substantiate the views expressed by M. Boucher de Perthes relative to the existence of the works of man associated with the remains of extinct animals in ground which has never been artificially disturbed, and belonging to strata of the Pleistocene period, irrespective of slight differences of age amongst the beds themselves, if any such really exist.

It may be instructive to inquire on what grounds this discovery and other analogous cases have been so long considered inadmissible as scientific facts. I have already noticed some criticisms called forth by M. Boucher de Perthes' work. One great cause of its neglect must have arisen, I conceive, from the injustice which the plates do to the objects described. The sketches of the implements are mere outlines of greatly reduced size, so that it is really often difficult to detect any definite shape or form even in those which belong to his group of hatchets. This, without a knowledge of the objects and of the localities, must have led, both in France and this country, to their being considered by many as merely chance forms of flints. It was probably this circumstance which caused Dr. Mantell*, from his not having seen the original specimens, to rank these discoveries as amongst the many cases of mistaken observation and determination. While admitting the value of his antiquarian labours, Dr. Mantell considered that M. de Perthes had not made himself sufficiently acquainted with geological phenomena, and observed "that the so-called works of art, figured and described by M. Boucher de Perthes, are nothing more than accidental forms of pebbles and stones, similar to those that occur in strata of immense antiquity, and which never can have been fashioned by the hand of man."

In the case of the occurrence of flint-implements in Kent's Hole, as discovered by the Rev. Mr. M'Enery, attested by Mr. Godwin-Austen, and by Mr. Vivian† and the Torquay Natural History Society, I do not see the grounds on which the evidence was

* *Opus cit.* p. 4.

† Quart. Journ. Geol. Soc. vol. iii. p. 353.

objected to, except that the fact was considered impossible and the chances of error great. It was not, I believe, controverted upon any specific grounds.

With regard to the remarkable case of the Liége caverns, Dr. SCHMERLING being a proficient comparative anatomist, his opinion necessarily attracted considerable attention, and a report on his work was presented to the "Académie des Sciences" by M. GEOFFROY ST.-HILAIRE*. Dr. SCHMERLING considered that the one sufficiently perfect skull found with the bones of the extinct animals was of a low order, and suggested that it resembled rather the skull of an Ethiopian than that of an European: he further expressed an opinion, that the human bones, together with the flint- and bone-implements discovered in these caves, belonged to a race of antediluvian men†. M. GEOFFROY ST.-HILAIRE, than whom there could not have been a better judge, looking apparently at the question from this point of view only, came, no doubt justly, to the conclusion that these presumed fossil skulls presented no greater deviation from the present type than might be found in many varieties of the Caucasian race now living. Whence it being inferred that the two skulls were those of existing man, and therefore, though ancient, not of Pleistocene date, Dr. SCHMERLING'S opinion failed to obtain acceptance. But it seems to me that it was judging the question on what in law term is called "a false issue;" for the main question was not whether we here had an extinct species of man, but whether these skulls, being those of man, were actually in true association with the remains of extinct animals. It does not follow, nor did M. SCHMERLING insist, that because the animals were extinct, any race of man occurring with them must also be of an extinct species.

I notice these few cases to show that it may in some instances be necessary to revise the opinions which have been passed on these and many other more or less probable cases, and that we may have to reconsider much of the evidence afresh.

§ 5. PARTICULARS REGARDING HOXNE.

On my return from France, my attention was directed by Mr. EVANS to another case of a very remarkable character, described, so far back as the first year in this century, in a paper of great value for the independent and corroborative evidence it affords, and for the bold and suggestive views of the author. Although known to antiquaries, its geological bearings had escaped notice. It relates to a discovery made, and communicated to the Society of Antiquaries, by Mr. JOHN FRERE, F.R.S., F.S.A.‡, under

* Comptes Rendus, vol. xvii. p. 13, 1838. † *Op. cit.* vol. ii. p. 178–9.

‡ Specimens of the Hoxne flint-implements have been preserved in the British Museum, and in the collection of the Society of Antiquaries. They closely resemble the French specimens. There is also in the British Museum another single specimen, singularly like some of the sharper-pointed specimens from Amiens. Respecting this specimen, I am indebted to Mr. FRANKS for the following particulars:—"Catalogue of Sloane Collection, No. 246—A British weapon found, with Elephant's tooth, opposite to Black Mary's near Grayes Inn Lane.—Conyers. It is a large black flint shaped into the figure of a spear's point—K." N.B. K probably means that this object was formerly in KEMP'S Collection (before 1715).

the title of "Account of Flint Weapons discovered at Hoxne in Suffolk*." The author stated that these weapons were found "in great numbers at a depth of about 12 feet," in a "stratified" gravelly soil underlying a layer of sand, containing shells and "some extraordinary bones, particularly a jaw-bone of enormous size of some unknown animal, with the teeth remaining in it." He also observed that the flint-weapons were so abundant, that they were used to fill in the ruts of the adjoining road. Mr. FREERE's further observations show that he was of opinion that the ground was undisturbed, and that the strata had been partially denuded; and he considered that the specimens must be of very great antiquity,—possibly "*even beyond that of the present world.*" Excellent plates of two flint-implements, singularly like the lance-shaped specimens from Amiens, accompany the paper.

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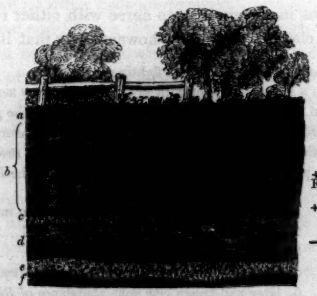
I lost no time in visiting Hoxne, a pretty village five miles eastward of Diss (Map, Plate XI.). The old brick-pit is about half a mile south of the village, on the road to Eye, adjoining the park and on the property of Sir EDWARD KERRISON. It is still worked, but the section is necessarily in some degree altered from what it was in Mr. FREERE's time. (For section of pit, see Plate XI. sect. 2.) The present diggings show:—

Section in S.W. corner of Hoxne brick-field, 1859.

Fig. 12.



	feet.
a. Surface soil, traces of sand and gravel...	1 to 2
b. Brown and greyish clay, not calcareous, —used for brick-earth; with an irregular central carbonaceous or peaty seam. Two flint-implements are marked in the position assigned to them by the workmen, by whom they were found last winter†	10 to 12
c. Yellow sub-angular flint-gravel, with a certain proportion of small chalk pebbles, and a few pebbles of siliceous sandstone, quartz, and other old rocks. Bones of Mammalia. The matrix of this bed, in places, consists of clay like *b*. It thins out to the westward	½ to 1
d. Bluish and grey calcareous clay, in places very peaty; lower part with seams or partings of sand. *Wood* and vegetable remains. Land and freshwater *shells*. Bones of *Mammalia*...	3 to 4
e. Gravel like *c*, but smaller, more worn, and with more chalk pebbles	1 to 2½
f. Calcareous grey clay, more or less peaty, with freshwater *shells* (I had a boring made in this bed to a depth of 17 feet, but no bottom was reached).	

I was fortunate in meeting with an old man who had worked in the pit since 1801.

* Archæologia, vol. xiii. p. 204, 1800. The original paper is as short as it is interesting.

† On my first visit I found no organic remains in this bed. The remains of the *Bos* (*primigenius*?) have since been found in it by the Rev. Mr. GUNN. And I have part of the socket of the tusk of an Elephant from the gravel *c*. These have been obligingly determined by Mr. QUEKETT (Nov. 1860).

On showing him a small ovoid flint-implement from Abbeville, he stated that many similar stones were formerly met with here, but that they were larger and more pointed*. Such specimens were now rare; only two had been found, at a depth of 7 and 10 feet from the surface in the clay (*b*), in the course of the preceding winter, and they had not been kept. However, after a short search in a rubbish heap, the men recovered one specimen†. Both in the gravel *c* and in the clay *d* bones of mammalia are still not unfrequently met with. I obtained a fragment of a rib of a Deer and part of the tooth of a Horse, and I afterwards saw, in the collection of Mr. T. Amyot‡ of Diss, the astragalus of an Elephant, which from the matrix in its interstices evidently came from the bluish calcareous clay *d*. Pieces of wood, some of considerable size, are found in this latter bed. Amongst them may be recognized species of Oak, Yew, and Fir; together with small seed-vessels. In the lower part of this bed are thin seams or partings of sand full of shells, perfect but very friable, of the following recent land and freshwater species§:—

Cyclas cornea, Linn.?	*Helix nitidula*, Drap.?	*Planorbis albus*, Müll.?
Pisidium amnicum, Müll.	—— *hispida*, Linn.?	—— *spirorbis*, Linn.
Unio (fragmentary).	*Limneus palustris*, Linn.	*Succinea putris*, Linn.
Bithinia tentaculata, Linn.	—— *truncatulus*, Linn.?	*Valvata piscinalis*, Müll.

According to Mr. Frere, the Flint-implements were discovered in gravelly soil underlying sand with shells and bones, and overlying a peaty clay. This would seem in some, but not in all respects, to agree with either *c* or *e* of the present section. Both overlie peaty clays‖. The men, however, say that it is not in those beds, but higher up (in *b*)

* The men here call them "fighting stones."

† On a subsequent visit with Mr. Evans we were more successful. We had a trench dug, on the east of the field, to the depth of 11 feet, and in examining the ground as it was thrown out by the men, Mr. Evans discovered in the bed of gravel, No. 4, a flint-implement perfect except the point, which had been broken off by the pick of the workmen and could not be recovered. This trench, which was of further importance as proving the superposition of these beds to the Boulder Clay, gave the following section:—

	ft.	in.	
1. Ochreous sand and gravel, passing down into white sand	4	9	10 feet.
2. Seams of fine white and ochreous gravel	1	3	
3. Light grey sandy clay	0	8	
4. Coarse yellow gravel in which the *flint-implement* was found	1	0	
5. Grey and brown clay with abundance of *Bithinia*	2	4	
6. Boulder Clay	1	0	

‡ I am much indebted to this gentleman's kind assistance and co-operation on my several visits to these pits.

§ The late Mr. John Brown, of Stanway, aided me in this collection. Most of the shells are so fragile and difficult to obtain perfect that several species have not yet been well determined.

‖ My first impression was in favour of *e*: still there is an objection to placing them in gravel; for why, in that case, should they have been picked out to mend the roads with? The gravel itself would have been used as it was. It would rather seem from this that they were flints found accidentally in a bed of clay or sand, which was worked as such, and the flints picked out and thrown on one side. It is, however, possible that *c* may have been more argillaceous and overlaid by a local bed of sand (No. 3 of Mr. Frere) with shells and bones, for beds of this character are liable to considerable changes, both in thickness and composition, within very short distances (Oct. 1860).

that they now find the flint-implements*. The gravel *e* is below all the beds worked. I had an excavation made in it, but without success; nor was my search in the other beds more successful on my first visit.

The Flint-implements I have seen in the collection of Mr. AMYOT and elsewhere, as well as those figured by Mr. FRERE, possess the same general characters, being rude, lance-shaped, and closely resembling one form from Amiens, only they are generally rather more slender and elongate (fig. 6, Plate XIV.).

The general evidence of this case certainly wants the completeness which the French deposits afford, but still there is every reason to believe it to be an analogous case. Unfortunately, the old part of the pit is now worked out and overgrown, but it is to be hoped that a full and efficient exploration of this interesting spot may some day be made. Mr. EVANS and I had several trenches dug, but much more is yet required. In one on the south side of the field, the brick-earth (*b*) was only 4 feet thick, and was overlaid by 3 to 4 feet of ochreous drift sand and gravel, and underlaid by 2½ feet of small gravel (composed in great part of small chalk pebbles) resting upon a grey clay. The other trench, on the east side, exhibited a bed of yellow sand with a few flints, 3½ feet thick, passing into ochreous gravel 1 foot, and under it a seam of grey clay 1 foot thick, and then another bed of gravel, at the top of which we were stopped by water. At a distance of 150 yards from this spot, and on the other side of the small stream, is a pit in which the Boulder Clay is dug and where no other beds are exposed.

This Boulder Clay caps all the hills around and forms a low table-land, through which the small valleys are cut. Its very uneven base rests on white and yellow sands and gravel (5). In places, however, thick beds of ochreous and ferruginous subangular flint-gravel, with subordinate beds of sand, form low hills subtending the main plateau along the valley of the Waveney. This gravel (2) is newer than the Boulder Clay against which it usually slopes off, running, in thin patches, up some of the lateral valleys (see Plate XI. sect. 3).

The top of the freshwater deposit of Hoxne reaches within 6 or 8 feet of the summit of the hill, of which it forms an unbroken and uniform part. The adjacent hills are of about the same height, and there is no ground above a few feet higher for some miles around. No existing drainage, nor any possible with this configuration of surface, could have formed these clay and gravel beds, at the relative level they now occupy†.

The presence and abundance of perfect shells of *Valvata* and *Bithinia*, and the quantity of vegetable matter, render it probable that these beds were accumulated by a slow stream, or in a small marshy lake or mere, into which land shells, the remains of land

* Other specimens have since been found in the lower part of *b*, and one in the gravel (probably *e*). 1860.

† Since writing the above, I have had the pit, and the intermediate ground to the Waveney, levelled. The top of the pit proves to be 42 feet above the adjacent brook, 53 feet above the Waveney, and 112 feet above the sea. With Sir EDWARD KERRISON'S courteous permission, we also had several trenches dug in the park to trace the extension of the Freshwater Deposit. The results of these operations are embodied in the plans and sections, Plate XI. Altogether there have been sixteen trenches and borings made in and around the pit.—October 1860.

animals, and drifted wood were carried down. The materials of this freshwater deposit are mainly such as would be produced and sorted by the slow wearing away of the Boulder Clay. The clays and marls, and the associated flint-gravels, with the pebbles of chalk, of quartz, and of hard sandstone, are materials just such as the artificial washing of the adjacent boulder clay now produces in the same field—a pure calcareous clay on the one hand, and a heap of rough gravel of flints, and older rock pebbles, on the other. The level of the Boulder Clay in the adjacent field is lower than the brick-pit, whilst elsewhere around it rises higher. The irregular patches of sand and gravel on the top of the whole are not of local origin, but belong, I believe, to the general superficial drift of the district. A portion of the freshwater deposit has suffered denudation,—a denudation evidently of the date of that which formed the small valley running down by Hoxne to the Waveney, and connected with the general valley system of the district.

This Hoxne section furnishes us with an important clue to the relative age of these several flint-implement-bearing deposits. As far as we can now judge, it is clearly newer than the Boulder Clay, and is probably older than some portion of the superficial sands and gravels. Probably of the same age, and much resembling the Hoxne deposit in many of its details*, are the deposits at Mundesley, Copford, Lexden, and others in the South of England. They were all formed before the country had assumed exactly its present form of surface,—before all its variety of hill and dale had been fashioned to their present shape. Even should the exact position of the worked flints at Hoxne prove to be above all the bone-bearing beds, and not in them, still that they are contemporaneous with an old condition of surface, and that over the whole is spread a drift concomitant with a modification of that surface, and giving the stamp to some of the present minor features of the country, is in either case, a very remarkable fact.

§ 6. GENERAL CONCLUSIONS.

From the foregoing considerations I cannot do otherwise, concerning the material facts, than come to the conclusions, agreeing essentially with M. Boucher de Perthes and Dr. Rigollot†, that—

1st. The flint-implements are the result of design and the work of man.

2ndly. That they are found in beds of gravel, sand, and clay which have never been artificially disturbed.

3rdly. That they occur associated with the remains of land, freshwater, and marine Testacea, of species now living and most of them yet common in the same neighbourhood, and also with the remains of various Mammalia,—a few of species now living, but more of extinct forms.

* In company with Mr. Evans, I have since found a similar freshwater deposit at Athelington, in the same valley as, and five miles S.S.E. from, Hoxne. The deposit, although small, is interesting from the circumstance of the Boulder Clay being seen to pass under it, and from its being overlaid by 8 feet of ochreous gravel and sand.—September 1860.

† On the theoretical questions I differ materially from these gentlemen. I consider the Diluvial theory, as interpreted by them, to be inadmissible.

And further, 4thly. That the period at which their entombment took place was subsequent to the Boulder Clay period, and to that extent post-glacial; and also that it was amongst the latest in geological time,—one apparently immediately anterior to the surface assuming its present form, so far as it regards some of the minor features.

It is true that no remains of Man himself have yet been found,—that is still to be desired; but if it be admitted that the flint-implements are his work, the negative point becomes an argument of less value.

Whilst abstaining from any general hypothesis in explanation of the phenomena, there is, however, one point to which I must refer before concluding, although I cannot, at present, venture beyond a few generalities respecting it. It might be supposed that in assigning to Man an appearance at such a period, it would of necessity imply his existence during long ages beyond all exact calculations; for we have been apt to place even the latest of our geological changes at a remote, and, to us, unknown distance. The reasons on which such a view has been held have been, mainly,—the great lapse of time considered requisite for the dying out of so many species of great Mammals,—the circumstance that many of the smaller valleys have been excavated since they lived,—the presumed non-existence of Man himself,—and the great extent of the later and more modern accumulations. But we have in this part of Europe no succession of strata to record a gradual dying out of the species, but much, on the contrary, which points to an abrupt end, and evidence only of relative and not of actual time; while the recent valley-deposits, although often indicating considerable age, show rates of growth, which, though variable, appear, on the whole, to have been comparatively rapid. The evidence, in fact, as it at present stands, does not seem to me to necessitate the carrying of man back in past time, so much as the bringing forward of the extinct animals towards our own time; my own previous opinion, founded upon an independent study of the superficial drift or Pleistocene deposits, having likewise been certainly in favour of the latter view. There are numerous phenomena, which I can only consider as evidence of a sudden change, and of a rapid and transitory action and modification of the surface, at a comparatively recent geological period—a period which, if the foregoing facts are truly interpreted, would seem nevertheless to have been marked, before its end, by the presence of Man, on a land clothed with a vegetation apparently very similar to that now flourishing in like latitudes, and whose waters were inhabited by Testacea also of forms now living; while on the surface of that land there lived Mammalia, of which some species are yet the associates of man, although accompanied by others, many of them of gigantic size, and of forms now extinct.

APPENDIX.

(A.) Letter from JOHN EVANS, Esq., F.S.A., F.G.S., to the author, *on the Form and Nature of the Flint-implements.* Dated,—Nash Mills, Hemel Hempsted, May 25, 1859.

MY DEAR SIR,—In accordance with your wish I send you a few notes upon the flint-implements, or weapons discovered in the beds of drift which we lately visited together in the neighbourhood of Abbeville and Amiens, regarding them from an antiquarian rather than a geological point of view.

What appears to me of most importance, is to point out wherein these implements from the drift resemble or differ from those in some degree analogous with them, which are so frequently found in this country and on the Continent, and are usually considered to be the work of the primitive, or as for convenience sake I will call them, the Celtic inhabitants of this part of Europe.

The resemblances and differences may consist in material, form, or workmanship, and on each of these points I will say a few words.

1st. As to the material from which they are formed,—the flints derived from the chalk. This is the same as has been so extensively employed for the manufacture of weapons and implements by uncivilized man in all ages and in all countries where flints are to be found; the hardness of the stone and the readiness with which it may be fractured in such a manner as to produce a cutting edge, giving it a preference over all other stones, and in some instances having caused it to be sought for at a distance, when not found upon the spot, for the purpose of converting it into knives, axes, or arrow-heads. There is, however, this to be observed about the weapons or implements from the drift, that though they are found in a country abounding in flint, the stones from which they were formed do not appear to have been so carefully selected, nor to have been as free from flaws and imperfections as those employed for a similar purpose by the Celtic tribes. These latter also not unfrequently used other stones, as greenstone*, syenite, porphyry, quartz, jade and serpentine, as materials for weapons or tools, but those from the drift are, as far as has hitherto been ascertained, exclusively of flint.

2. As to form, there is for the most part a marked difference between the worked flints from the drift and those of the ordinary Stone period. The former may, for my present purpose, all be grouped under three heads:—

1. Flint flakes, apparently intended for arrow-heads or knives.
2. Pointed weapons, analogous to lance or spear heads.
3. Oval or almond-shaped implements presenting a cutting edge all round.

It is in the first-named class of implements *only* that there is any close analogy with those not unfrequently found with other remains of human art, which are considered to belong in this country to a period but slightly prehistoric. Wherever flint is used as a material for the formation of tools or weapons, many of the flakes or splinters arising from the chipping of the flint, will of necessity present sharp cutting edges, and are certain in consequence to be utilized. These flakes seem peculiarly well adapted for points of darts or arrows, or for cutting purposes, and for such have been used in all ages. But the very simplicity of their form prevents those fabricated at the earliest period

* Arch. Assoc. Journal, vol. ix. p. 65.

from being distinguishable from those of a later date; and as they are often produced even by a single blow, it is at all times difficult to discern those formed by the hand of man from those resulting from the accidental fracture of a flint by natural causes. For this reason, mere flakes of flint, however analogous to those we know to have been made by human art, can only be regarded as affording doubtful evidence of man's existence, unless found in sufficient quantities to prove design in their formation. The flint flakes you found in the sand at Menchecourt are in my opinion the work of man, as are also those found in some of the ossiferous caverns both in England and on the Continent; but granting them to be so, there is little or nothing in their form to distinguish them from those with which we are already acquainted.

The case is different with the implements of the second class—those resembling spear or lance heads in form. Of these there are two varieties; the one rounded at the point, its outline presenting a sort of parabolic curve; the other acutely pointed, with the sides curved slightly inwards. The edges of both kinds are to a certain extent made sharp, but not so much so as the points, and altogether they appear better adapted for piercing than for cutting. Both shapes are usually truncated at the base, and at that end frequently show the original form of the flint. It is of course impossible to say for what purpose they were intended; but they may have been attached to the end of poles so as to form spears or darts, or used without any handle for grubbing in the ground, or as wedges for splitting wood. I know of no analogous form among the Celtic implements; some of the rudely chipped arrow-heads found in Ireland and elsewhere present the nearest approach to it, but are far smaller in size, the weapons from the drift being usually from 5 to 6 inches in length. The ordinary form of stone celt is, as you are aware, intended for cutting at its broad end, the narrow end being inserted in the socket of the handle; these, on the contrary, cut or pierce at the narrow end, while the broad end appears intended to rest against a stop or bracket, or to be held in the hand.

The third class, implements with a cutting edge all round, have also no correspondence with the usual forms. Their prevailing shape is an oval, more or less pointed at one end, and equally convex on both sides. They vary in length from 2 to 8 inches, but are usually from 4 to 6 inches long. There is also considerable variety in their form, probably owing to defects in the flints from which they were fashioned; and in fact the two classes into which, for convenience sake, I have divided these rudely-formed instruments, as distinct from the flint flakes, may be said to run one into the other; it being hard to determine to which of them some of the weapons are to be referred. Such of the Celtic implements as have a cutting edge all round, are more triangular in their form and are of very rare occurrence; those of the oval-shape, on the contrary, appear to be equally common in the drift with those of the spear head character, the oval form predominating near Abbeville, and the spear heads being most abundant at St. Acheul. The use for which they were intended is by no means apparent. They may, however, have been used as axes, or those of the smaller size possibly as sling-stones propelled either from the ordinary sling or the end of a cleft stick.

3. In point of workmanship, the implements of the two classes last described differ from those of the ordinary Stone period in several particulars. The majority of the latter show traces of having been ground and polished, wholly or in part; those from

the drift, on the contrary, have merely been roughly chipped out of the flint, and in no case ground. When from any cause the former have been left as originally chipped out, it will be found in most instances that the chipping process has been executed with much greater nicety, and the chips or splinters removed have been much smaller than those from the weapons found in the drift. Rude as the ordinary stone implements may appear, they seem to point to a higher degree of civilization than those I am now considering. Who the people were that formed them, at what period they lived, and in what manner these their memorial stones became imbedded in the mass of drift in which they are now discovered, must, I am afraid, ever remain a matter for conjecture. But that these weapons and implements form as much an integral part of the deposit in which they are found as any other of its constituent flints or pebbles, I for one am convinced. The undisturbed state of the beds of sand and gravel, the incrustations upon some of the worked flints (identical with that upon the other flints in the same bed, a really antique patina), the concurrent testimony of the workmen, the similarity of the discoveries at Abbeville and Amiens, thirty miles apart, the assurances of M. Boucher de Perthes, both verbal and printed, and lastly, our own observations, all convinced me that they were not at any subsequent period buried in the gravel, but were entombed in it with the remains of the Elephant, Rhinoceros, and other extinct mammalia, at the time when the agent was still in force by which these beds of drift were deposited. Had any doubts remained upon my mind, the discovery of identical weapons at Hoxne in Suffolk, in conjunction with similar remains of extinct mammals and in analogous drift, recorded moreover in the 'Archæologia' sixty years ago by an antiquary unfettered by geological theories, would have sufficed to have removed them. There appear to have been one or two other similar discoveries in England, and more would probably have been recorded, had not the rudeness of the workmanship of the weapons been such that they would hardly attract the eye of an ordinary observer, while those scientific persons who have been engaged in the investigation of the drift, have been more on the alert for fossil organisms than for traces of the hand of man. These diluvial beds will, however, now form a point of union on which both the geologist and the antiquary may prosecute their inquiries together; and on this neutral territory between Palæontology and Archæology a wide field is opened for investigation, which must eventually lead to a great extension of our knowledge of the history of primeval Man.

Believe me, my dear Sir, ever yours sincerely,

John Evans.

(B.) Extract from letter of Dr. H. Falconer, F.R.S., F.G.S. &c., to the author, *descriptive of the result of his recent examination of the remains of the great extinct Pachyderms in the several collections at Amiens.* Dated Lyons, 21st October, 1860.

"1. In M. Garnier's private collection I saw two well-marked examples of molars of *Elephas antiquus*; the one a magnificent specimen of the last true molar, lower jaw left, composed of fourteen collines to the crown, all more or less worn. The characters are so pronounced that I would have selected it as a typical illustration of the species for a drawing. The specimen was stated by M. Garnier to be from St. Roch. There was one peculiarity about it deserving consideration, that tested by '*l'happement à la langue*;'

it was highly absorbent, *i. e.* cleared out of its gelatine. It was in several pieces, but the outer layer of cement was entire, and the specimen as a whole bore no indications of having been rolled along with gravel.

"2. In the same collection, a very fine first true molar, upper jaw, also of *Elephas antiquus*, composed of the eight anterior collines; the talon and two front ridges worn, the rest intact. The crown completely denuded of the shell of enamel, and *may have been rolled*; mineral condition *highly absorbent*. This specimen, M. GARNIER informed me, came out of the same deposit as 'les haches,' *i. e.* St. Acheul.

"3. Museum of the Jardin des Plantes. A very fine series of molars and other remains of *Elephas primigenius*, from the gravel of St. Roch. In mineral condition wholly different from No. 1, *i. e.* the enamel *glistening and pearly* like that of a modern tooth; plenty of gelatine, and no great '*happement à la langue*.' They are reputed to be from the gravel deposit of St. Roch. The surface white, as if out of chalk rubble.

"4. Among these were two superb last lower molars of *Elephas primigenius*, one of them perfectly entire, and a model specimen for an illustration. The outer shell of cement of these specimens, although in the fossil state, a soft tender material, which readily yields to '*frottement*' when rolled with gravel, was perfectly entire, just as if it had been imbedded in a tranquil lacustrine deposit. At the Jardin des Plantes I saw not a trace of *Elephas antiquus*, either from St. Roch or St. Acheul.

"The other principal remains in the same collection were of *Rhinoceros tichorhinus*, lower jaws and molars, upper and lower; not a trace did I see either of *Rhinoceros hemitæchus* nor of *Hippopotamus major*; and if I remember right, the tusks which you had of the latter form, adhered strongly to the tongue."

(C.) Extract from letter of M. BAILLON to Dr. RAVIN (*op. cit.*) in Mém. Soc. Roy. d'Emulation d'Abbeville for 1834–35, p. 197.

"On commence à trouver des ossemens à 10 ou 12 pieds de profondeur dans les sables de Menchecourt; mais on en trouve une bien plus grande quantité à 18 et 20 pieds. Il y a de ces ossemens qui furent brisés avant d'être enfouis et d'autres dont les angles sont arrondis sans doute parce qu'ils ont été roulés par les eaux; mais ils ne sont pas enterrés aussi profondément que ceux qui sont demeurés intacts. Ceux-là sont déposés au fond de la sablière: ils y sont entiers, sans brisure ni frottement, et il est probable qu'ils étaient encore articulés quand ils ont été recouverts. J'y ai trouvé tout un membre postérieur de rhinocéros dont les os étaient encore dans leur situation relative ordinaire: ils ont dû être joints par des ligamens et même entourés de muscles à l'époque le leur enfouissement. Le squelette entier du même animal gisait à peu de distance."

(D.) Extracts from letter of M. BOUCHER DE PERTHES, President Soc. d'Emul. Imp. d'Abbeville, to the author, on his request for *a rough approximate estimate of the number of Flint-implements (Haches) found near Abbeville.* Dated November 1860.

"Il m'est bien difficile de vous dire combien j'ai trouvé de haches.....Mes reponses sur le nombre des haches de chaque localité ne sont que des indications."

"Les haches bien caractérisées ont toujours été rares à Menchecourt; je n'en ai pas trouvé moi-même plus d'une douzaine, et les ouvriers ne m'en ont pas apporté plus d'une quarantaine, peut-être moins. Si vous admettez que ces ouvriers ont porté ailleurs une trentaine d'autres haches, vous arrivez à presqu'une centaine recueillie en 20 ans.

"A St. Gilles elles sont encore plus rares; j'en ai trouvé une vingtaine de roulées et très grossières, mais de bien faites pas plus que 10 à 12; les ouvriers peut-être en ont ils recueilli autant.

"A Moulin Quignon on en a trouvé accidentellement quelques douzaines; puis on est resté des mois, des années, sans en trouver une seule: je ne parle pas des roulées et très grossières, on en trouve toujours. J'estime de 150 à 200 haches bien taillées celles qui y ont été recueillies; dont une trentaine par moi, dont il n'y a que 7 à 8 de bien taillées; la plûpart des autres ont été trouvées devant moi: quand je n'étais pas là les ouvriers ne les voyaient pas, ou ne les ramassaient pas, et après le travail je les recueillais dans la tranchée ou dans les tas de silex amoncelés sur les bords.

"Quand plus tard on fit les travaux du Champ de Mars ..... une vaste partie du banc diluvium fut mis à découvert: là on trouva des haches par centaines—400 à 500, peut-être plus.

(E.) I am indebted to Mr. RUPERT JONES and Mr. PARKER for an examination of the sands and clays of the Abbeville and Amiens deposits, in order to determine whether they contained microscopic entomostraca or foraminifera. With the exception of one doubtful specimen, they found no recent forms, but the list of derived specimens is interesting.

AMIENS.		ABBEVILLE.	
c. Sand. St. Acheul.		*c*. Loam. Menchecourt.	
Rotalia Clementiana, d'Orb.	Chalk.	*Rotalia Corderiana*, d'Orb.	Chalk.
Cytherella ovata, Rœmer.		*Rotalia Clementiana*, d'Orb.	
Rotalia ammonoides, var., Reuss.	Tertiary?	*Rotalia umbilicata*, d'Orb.	
Candona, sp. (recent?)		*Rotalia ammonoides*, var. Reuss.	Tertiary.
d. Gravel. St. Acheul.		*d*. Sand. Menchecourt.	
Rotalia Clementiana, d'Orb.	Chalk.	*Rotalia Clementiana*, d'Orb.	Chalk.
Bulimina variabilis, d'Orb.		*Rotalia Micheliniana*, d'Orb.	
Cytheridea Muelleri, Munst.	Tertiary.	*Rotalia umbilicata*, d'Orb.	
Cythere scrobiculata?, Münst.		*Bulimina variabilis*, d'Orb.	
Polystomella crispa, Linn.		*Cristellaria rotulata*, Lamarck.	
		Rotalia Beccarii, Linn.	Tertiary.

From the Foraminifera and Entomostraca above enumerated, it appears that the sands, &c. referred to, were mainly derived from the chalk, and received additional materials from some tertiary beds.

(*a*—*f*). 6 Foraminifera from chalk (11 occurrences)	Chalk 12 occurrences.
(*x*—*y*). 3 Foraminifera from tertiary sources (4 occurrences)	
(1). 1 Entomostracon from chalk (1 occurrence)	Tertiary 7 occurrences.
(*i*—*iii*). 3 Entomostraca from tertiary sources (3 occurrences)	

(In some of the clays and gravels of Hoxne I have also seen derived or extraneous Foraminifera, but they yet require working out.—J. P.)

(F.) Levels around Abbeville referred to in the paper. As the mètres are there reduced to English feet, I here give the copy of the original document, for which I am obliged, through M. Boucher de Perthes, to the Engineers "des Ponts et Chaussées."

Designation des Carrières.		Plus hautes eaux de retenues artificielles de la Somme en 1837.	Hautes eaux extraordinaires de la Somme en 1841.	Marées extraordinaires de vives eaux au port de St. Valery.	Niveau moyen de la Mer à St. Valery sur Somme.	Niveau moyen de la Mer au Hâvre.
		mètres.	mètres.	mètres.	mètres.	mètres.
Carrière de cailloux à l'extrémité, côté gauche, du faubourg St. Gilles	Terrain naturel au sommet de la Carrière	21·95	21·41	20·55	27·02	29·16
	Partie nivelée du terrain exploité	19·95	19·41	18·55	25·02	27·16
Carrière de cailloux de la porte du bois près le Moulin Quignon	Terrain naturel au sommet de la Carrière	27·15	26·61	25·75	32·22	34·36
	Partie nivelée du terrain exploité	25·15	24·61	23·75	30·22	32·36
Sommet de la butte du Moulin Quignon		31·11	30·57	29·71	36·18	38·32
Carrière de sable de Menchecourt appartenant aux Srs Dufour et Coulombel	Terrain naturel au sommet de la Carrière	12·97	12·43	11·57	18·04	20·18
	Partie nivelée du terrain exploité et en culture	7·77	7·23	6·37	12·84	14·98
Tertre sur lequel est placé le moulin de l'argillière (Menchecourt)		51·49	50·95	50·09	56·56	58·70

Sablières* appartenant au Sr Papillon situées à Mautort à gauche de la route impériale No. 25 à l'entrée de celle qui conduit à Gamaches — Le centre de cette carrière se trouve à 6 mètres au dessus du niveau de la mer au Hâvre. (It is 2·50 mètres more to the top of the pit.)

Le niveau moyen de la Somme est à 6·10 mètres au dessus du niveau de la mer au Hâvre.
Le niveau de la vallée près la station du chemin de fer à Abbeville est à 7·60 mètres au dessus du niveau de la mer au Hâvre.

Levels around St. Acheul, from a ground plan obligingly furnished by M. Pinsard.

	mètres.	English feet.	
Valley of the Somme near La Neuville	20·42	67	These heights are above the mean tide at Hâvre. To reduce them to the mean tide at St. Valery, deduct 2·14 mètres, or 7 feet.
The railway at La Neuville	25·33	83	
Midway between La Neuville and St. Acheul	37·16	122	
High road, suburb of Amiens, at junction with the Cagny road	32·09	105	
High road, in front of the Monastery of St. Acheul	44·57	146	
Mean surface at T. and F. Freville's pits	47·50	156	
High road, opposite by-road leading to the Cagny road	42·15	138	
Cagny road, end of the preceding by-road	51·64	169	
On the Cagny road, 273 yards south-east of last point	56·88	187	
The highest point of the hill, 5 furlongs south of the pits, on the road to Cottenchy	66·10	217	

(G.) M. Boucher de Perthes has found that the silt and peat beds of the valley at Abbeville contain near the surface mediæval remains; lower Roman remains; and, beneath all, Celtic remains (*op. cit.* p. 182 to 206). A trench at La Portelette showed—

	ft.	in.	ft.	in.
1. Made ground and alluvial soil	10			
2. Calcareous tufa, with traces of plants and bones (a small statuette and Roman coins?)	6	6		
3. Bluish gray clayey sand, with ground flint and jade Implements, worked bones, and bones of Beaver, Bear, Boar, Deer, &c.	10		39	6
4. Peat, enclosing Celtic sepultures, coarse pottery, and rude bone and flint-implements	10			
5. Muddy sand and over flint gravel, reposing upon an irregular surface of chalk	3?			

At a short distance from Porte Mercadé the silt and peat with mediæval coins and Roman remains are 20 feet thick, and overlie 2 feet of muddy sand, containing a mass of rude flint-implements and coarse pottery.

Section by M. Pinsard of a boring in the valley of the Somme at Amiens.

1. Vegetable soil and silt, with bones of Deer, &c.	7	6	31 feet.
2. Peat	8	8	
3. Gravel, very similar to that of St. Roch and St. Acheul (newer, on my view.—J. P.)	14	10	

* This level was taken in error for one I wished to have of the pit where the flint-implements have been lately found, on the slope of the hill on the road to Moyenville (see "Pits," Section 1, Plate X.).

Explanation of Plates.

PLATE X.

A, B. Plans of the districts immediately around Abbeville and Amiens, showing the extent of the flint-implement-bearing deposits, and of the recent valley-deposits. The topographical part is copied from the French Ordnance Maps.

Outline map of part of the valley of the Somme, with some principal heights.

1, 3. Theoretical sections across the valley of the Somme at Abbeville and Amiens, showing the relative position and proportion of the beds, their relation to the present valley, and their level above the sea. (The gravel under the peat belongs to bed No. 1.)

2. Theoretical section through Abbeville parallel with the valley of the Somme.

PLATE XI.

Map of the district around Hoxne, showing the position and probable extent (the cross lines) of the flint implement-bearing deposit The ground plan copied from Ordnance Map.

1. Levels of the ground from the river Waveney* to the road by the side of Hoxne brick-field. The levels of this and the following section were taken by Mr. Alger of Diss.

2. Actual section across the Hoxne brick-field, showing the extent of the working, the relative position of the strata, and the relation of the deposit to the surrounding surface.

3. Theoretical section, showing the relation of the Hoxne deposit to the other strata of the district, and its conformity with the present surface.

PLATES XII. to XIV.

Specimens of the principal forms of Flint-implements: *a*, front view; *b*, side view.

From the neighbourhood of Abbeville,—1, 2 and 3 from the collection of M. Boucher de Perthes.

Fig. 1. St. Gilles, in ochreous gravel; depth uncertain; colour,—light opake yellow.

Fig. 2. Mautort, 1847; in marly gravel; depth uncertain; colour,—dull opake white; reverse side, flat, simple fracture.

Fig. 3. Menchecourt; in sand (marl seam) *d*?; depth 26 feet; outer surface decomposed to a porcelain white.

Fig. 7. Menchecourt, 11th April, 1859; in gravel *e* (fig. 2); depth 14 feet; original black colour of the flint unaltered; found by the author.

* The north end of this section is carried too far east on the Map. It should be direct along the road from B to A.

From St. Acheul, Amiens.

Fig. 4. Found in the gravel *d* (sect. 6, p. 289), April 1860; depth about 24 feet; a small flint, with a thick white crust, a large portion of which remains, chipped at one end only; colour unaltered.

Fig. 5. Found in the gravel *d* (section, p. 292, near spot where Mr. FLOWER and the author found their specimens), June 1859; depth about 20 feet; black flint, original colour unaltered; vitreous lustre.

Fig. 8. Found in the gravel *d*, April 1859; depth uncertain; one side clear and but little altered, the other side slightly stained yellow, and partially coated with a film of carbonate of lime.

From Hoxne . . . . . Fig. 6. Found in the brick-earth *b*, 1852; depth uncertain; from the collection of Mr. AMYOTT; surface but little altered; more vitreous than in a freshly broken flint.

Note.—On Plate XI., beds No. 2, section 3, are represented too thick, whilst the line of base of the Boulder Clay (4) should be more irregular and higher.

XVIII. *On the Formulæ investigated by Dr.* BRINKLEY *for the general Term in the Development of* LAGRANGE'S *Expression for the Summation of Series and for successive Integrations. By Sir* J. F. W. HERSCHEL, *Bart., F.R.S. &c.*

Received April 26,—Read June 14, 1860.

IN the Transactions of the Royal Society for 1807, Dr. BRINKLEY has investigated the general value of the coefficient of any term in the development of the function $\left(\frac{t}{e^t-1}\right)^n$, and his result is remarkable for the mode of its expression in terms of the successive differences of the powers of zero, or of the numbers comprised in the general expression $\Delta^m 0^n$. Since that time, in my paper published in the Transactions of the Society for 1815, "On the Development of Exponential Functions," I have exhibited other, and much more simple as well as more easily calculable expressions for the same coefficient, by means of the same useful and valuable differences, and in that and other subsequent memoirs, have extended their application to a variety of interesting inquiries in the theory of differences and series. It is singular, however, that up to the present time it has never been shown that the formulæ of Dr. BRINKLEY, and my own, though affording in all cases coincident numerical results, are analytically reconcileable with each other; nor indeed is it at all easy to see either from the course of his investigation, which turns upon an intricate application of the combinatory analysis, or from the nature of the formula itself, how it is possible to pass from the one form of expression to the other so as to show their identity. This is what I now propose.

Referring to my "Collection of Examples in the Calculus of Finite Differences*," will be found the following relation, which enables us to pass from the differences of any one power of zero, as 0^r, to those of any other, as 0^{r+n}, viz.—

$$\{\log(1+\Delta)\}^n . f(\Delta)0^r = x(x-1)\ldots(x-n+1) . f(\Delta)0^{r-n},$$

or changing x into $x+n$,

$$\{\log(1+\Delta)\}^n . f(\Delta)0^{r+n} = (x+1)(x+2)\ldots(x+n) . f(\Delta)0^r.$$

As this equation is general so long as negative indices of Δ do not occur, we may change $f(\Delta)$ into $\frac{f(\Delta)}{(\log(1+\Delta))^n}$, and it becomes

$$f(\Delta)0^{r+n} = (x+1)\ldots(x+n) . \frac{f(\Delta)}{\{\log(1+\Delta)\}^n} 0^r,$$

provided always that $\frac{f(\Delta)}{\Delta^n}$ contains no negative powers of Δ. In this for $f(\Delta)$ sub-

* Camb. 1820, p. 70. Ex. 6.

stitute Δ^{i+n}, and we have

$$\Delta^{n+i}0^{x+n}=\frac{[x+n]}{[x]}\,\Delta^i\left\{\frac{\Delta}{\log(1+\Delta)}\right\}^n 0^x=\frac{[x+n]}{[x]}\,\Delta^i\,\nabla^n 0^x;$$

denoting by $[x]$ the continued product $1.2.....x$, by $[x+n]$, $1.2.3...(x+n)$, and by ∇ the combination of operations expressed by $\frac{\Delta}{\log(1+\Delta)}$, that is to say, making

$$\nabla 0^x=\left(1-\frac{\Delta}{2}+\frac{\Delta^2}{3}-\frac{\Delta^3}{4}+\&c.\right)^{-1}$$

$$=1+\frac{\Delta}{2}-\frac{\Delta^2}{12}+\frac{\Delta^3}{24}-\&c.;$$

so that if we put $i=0$, we shall also have

$$\Delta^n 0^{x+n}=\frac{[x+n]}{[x]}\,\nabla^n 0^x,\quad\text{and}\quad\frac{\nabla^n 0^{x+n}}{[x+n]}=\frac{\nabla^n 0^x}{[x]}\quad.\quad.\quad.\quad.\quad.\quad.\quad(A.)$$

This premised, putting A_x for the coefficient of t^x in $\left(\frac{t}{e^t-1}\right)^n$, Dr. BRINKLEY's general formula for A_x* is as follows:—

$$A_x=-n.\frac{\overline{n+2}.\overline{n+3}....\overline{n+x}}{1.2.....(x-1)}.\frac{1}{1}.\frac{\Delta 0^{x+1}}{1.2...(x+1)}+n.\overline{n+1}.\frac{\overline{n+3}....\overline{n+x}}{1.2.....(x-2)}.\frac{1}{1.2}.\frac{\Delta^2 0^{x+2}}{1.2.....(x+2)}-\&c.,$$

or in our abbreviated notation,

$$A_x=-\frac{1}{1.(n+1)}.\frac{[x+n]}{[n-1].[x-1]}.\frac{\Delta 0^{x+1}}{[x+1]}+\frac{1}{1.2.(n+2)}.\frac{[x+n]}{[n-1][x-2]}.\frac{\Delta^2 0^{x+2}}{[x+2]}-\&c.,$$

which, in consequence of the equation (A.), will be transformed to

$$A_x=-\frac{1}{[n-1].[x]}\left\{\frac{[x+n]}{[x-1]}.\frac{1}{[n+1]}.2.3...n\nabla-\frac{[x+n]}{[x-2]}.\frac{1}{[n+2]}.3.4....(n+1)\nabla^2-\&c.\right\}0^x.\quad.\quad(B.)$$

Now we have

$$(1-\nabla)^{x+n}=1-\frac{x+n}{1}\nabla+\frac{(x+n)(x+n-1)}{1.2}\nabla^2,\ \&c.;$$

and therefore, putting S_n for the sum of the n first terms of this series,

$$(1-\nabla)^{x+n}-S_{n+1}=(-1)^{n+1}\left\{\frac{[x+n]}{[x-1]}.\frac{1}{[n+1]}\nabla^{n+1}-\frac{[x+n]}{[x-2]}.\frac{1}{[n+2]}.\nabla^{n+2}+\&c.\right\},$$

and consequently

$$\left(\frac{d}{d\nabla}\right)^{n-1}.\left\{\frac{(1-\nabla)^{x+n}-S_{n+1}}{\nabla}\right\}=(-1)^{n+1}\left\{\frac{[x+n]}{[x-1]}.\frac{2.3...n}{[n+1]}\nabla-\&c.\right\},$$

whence it appears that

$$A_x=(-1)^n.\frac{1}{[n-1].[x]}.\left(\frac{d}{d\nabla}\right)^{n-1}\left\{\frac{(1-\nabla)^{x+n}-S_{n+1}}{\nabla}\right\}0^x.$$

Dr. BRINKLEY's expression is therefore now divested of its form in which successive different powers of 0^x occur, and reduced to one in which, according to the spirit of the algorithm adopted in my system, successive powers of Δ, or of some functions of Δ

* Philosophical Transactions, 1807, p. 125.

(as ∇) only occur, applied all to one and the same power, 0^x; and it only remains to develope the function of ∇ we have arrived at in powers of Δ, bearing in mind that $\nabla = 1+\frac{\Delta}{2}-\frac{\Delta^2}{3}+$ &c., or $1-\nabla = \Delta\left\{-\frac{1}{2}+\frac{\Delta}{3}-\frac{\Delta^2}{4}+\text{ &c.}\right\}$.

Now as regards the term $\frac{(1-\nabla)^{x+n}}{\nabla}$, it is obvious that it will take when developed the form $\Delta^{x+n}.\{\alpha+\beta\Delta+\gamma\Delta^2+$ &c.$\}$, and therefore, that when differentiated $n-1$ times successively with respect to Δ, it will have the form $\Delta^{x+1}\{\alpha'+\beta'\Delta+\gamma'\Delta^2+$ &c.$\}$, so that, when applied as an operative symbol to 0^x, the result will be $=0$. This term then may be simply struck out, and we have only to consider the development in Δ of $\left(\frac{d}{d\nabla}\right)^{n-1}.\frac{-S_{n+1}}{\nabla}.0^x$.

Now this is equal to

$$-\left(\frac{d}{d\nabla}\right)^{n-1}.\left\{\frac{1}{\nabla}-(x+n)+\frac{(x+n)(x+n-1)}{1.2}\nabla-\ldots\pm\frac{[x+n]}{[n].[x]}\nabla^{n-1}\right\}0^x$$

$$=-\left\{\left(\frac{d}{d\nabla}\right)^{n-1}.\frac{1}{\nabla}-0+0+0\ldots\ldots\qquad\pm\frac{[x+n]}{n.[x]}\right\}0^x,$$

all the terms of which vanish except the first, x being >-1, and the whole reduces itself to $-\left(\frac{d}{d\nabla}\right)^{n-1}.\frac{1}{\nabla}0^x$, or to $(-1)^n.\frac{[n-1]}{\nabla^n}0^x$. And we therefore obtain, finally,

$$A_x=\frac{1}{[x]}.\frac{1}{\nabla^n}0^x=\frac{1}{1.2.\ldots..x}.\left\{\frac{\log(1+\Delta)}{\Delta}\right\}^n.0^x,$$

which is identical with that given in my paper above mentioned, equation (6), or in the "Examples," p. 82.

J. F. W. HERSCHEL.

Collingwood, April 20, 1860.

Note by A. CAYLEY, *M.A., F.R.S.*

The above formula (B.), substituting therein for A_x the value $\frac{1}{[x]}\nabla^{-n}0^x$, becomes

$$\nabla^{-n}0^x=-\frac{1}{[n-1]}\left\{\frac{[x+n]}{[x-1]}\frac{1}{[n+1]}2.3..n\,\nabla-\frac{[x+n]}{[x-2]}\frac{1}{[n+2]}3.4\ldots\overline{n+1}\,\nabla^2-\text{ &c.}\right\}0^x;$$

or, as this may be written,

$$\nabla^{-n}0^x=\frac{[x+n]}{[n-1]}\left\{-\frac{1}{[1][x-1](n+1)}\nabla+\frac{1}{[2][x-2](n+2)}\nabla^2-\text{ &c.}\right\}0^x;$$

or, inserting a first term which vanishes except in the case $x=0$, and which is required in order that the formula may hold good for this particular value,

$$\nabla^{-n}0^x=\frac{[x+n]}{[n-1]}\left\{\frac{1}{[0][x]n}\nabla^0-\frac{1}{[1][x-1](n+1)}\nabla+\frac{1}{[2][x-2](n+2)}\nabla^2-\text{ &c.}\right\}0^x;$$

where the series on the right-hand side need only be continued up to the term containing $\nabla^x 0^x$, since the subsequent terms vanish.

Now $\nabla^{-n}0^x$, or $\left(\frac{\Delta}{\log(1+\Delta)}\right)^{-n}0^x$, is equal to $[x]\times$coef. t^x in $\left(\frac{e^t-1}{t}\right)^{-n}$, and so $\nabla^n 0^x$, or $\left(\frac{\Delta}{\log(1+\Delta)}\right)^n 0^x$, is equal to $[x]\times$coef. t^x in $\left(\frac{e^t-1}{t}\right)^n$.

Hence, putting $\mathrm{R}=\frac{e^t-1}{t}$, the last-mentioned formula will be true if, as regards the term which contains t^x, we have

$$\mathrm{R}^{-n}=\frac{[x+n]}{[n-1]}\left\{\frac{1}{[0][x]n}\mathrm{R}^x-\frac{1}{[1][x-1](n+1)}\mathrm{R}^{x+1}+\frac{1}{[2][x-2](n+2)}\mathrm{R}^{x+2}-\&c.\right\},$$

the series on the right-hand side being continued up to the term in R^x. This formula is, in fact, true if R, instead of being restricted to denote $\frac{e^t-1}{t}$, denotes any function whatever of the form $1+bt+ct^2+\&c.$, and it is true not only for the term in t^x, but for all the powers of t not higher than t^x. And, moreover, R^{-n} may denote any positive or negative integral or fractional power of R. In fact, the formula (assuming for a moment the truth of it) shows that the expansion of any power whatever of a series of the form in question, can be obtained by means of the expansions of the successive positive integer powers of the same series: the existence of such a formula (at least for negative powers) was indicated by EISENSTEIN, *Crelle*, t. xxxix. p. 181 (1850), and the formula itself, in a slightly different form, was obtained in a very simple manner by Professor SYLVESTER in his paper, "Development of an idea of EISENSTEIN," Quart. Math. Journ. t. i. p. 199 (1855); the demonstration was in fact as follows, viz. writing

$$\mathrm{R}^n=(1+\overline{\mathrm{R}-1})^n=1+\tfrac{n}{1}(\mathrm{R}-1)+\tfrac{n.n-1}{1.2}(\mathrm{R}-1)^2+\&c.:$$

if we attend only to the terms involving powers of t not higher than t^x, the series on the right-hand side need only be continued up to the term involving $(\mathrm{R}-1)^x$, and the right side being thus converted into a rational and integral function of R, it may be developed in a series of powers of R (the highest power being of course R^x), and the coefficients of the several powers are finite series which admit of summation; this gives the required formula. But there is an easier method; the process shows that the series on the right-hand side, continued as above up to the term involving t^x, is, as regards n, a rational and integral function of the degree x; and by LAGRANGE'S interpolation formula, any rational and integral function of n of the degree x, can be at once expressed in terms of the values corresponding to $(x+1)$ particular values of n. The investigation will be as follows:—Let R denote a series of the form $1+bt+ct^2+\&c.$, and let R^n denote the development of the nth power of R, continued up to the term containing t^x, the terms involving higher powers of t being rejected. R^0, R^1, R^2, &c., and generally R^x, will in like manner denote the developments of these powers up to the term involving t^x, or what is the same thing, they will be the values of R^n, corresponding to $n=0, 1, 2, \ldots s$. By what precedes R^n is a rational and integral function of n of the degree x, and it can therefore be expressed in terms of the values R^0, R^1, R^2, $\ldots \mathrm{R}^x$, which correspond to $n=0, 1, 2, \ldots x$.

Let s have any one of the last-mentioned values, then the expression

$$\frac{n.n-1.n-2\ldots n-x}{n-s}\,\frac{1}{s.s-1\ldots2.1.-1.-2\ldots-(x-s)},$$

which, as regards n, is a rational and integral function of the degree x (the factor $n-s$, which occurs in the numerator and in the denominator being of course omitted), vanishes for each of the values $n=0, 1, 2, \ldots x$, except only for the value $n=s$, in which case it becomes equal to unity. The required formula is thus seen to be

$$R^n=\Sigma\left\{\frac{n.n-1.n-2\ldots n-x}{n-s}\,\frac{1}{s.s-1\ldots2.1.-1.-2\ldots-(x-s)}\,R^s\right\},$$

where the summation extends to the several values $s=0, 1, 2\ldots x$; or, what is the same thing, it is

$$R^n=\Sigma\left\{\frac{n.n-1.n-2\ldots n-x}{n-s}\,\frac{(-)^{x-s}}{1.2\ldots s.1.2\ldots(x-s)}\,R^s\right\};$$

or changing the sign of n, it is

$$R^{-n}=\Sigma\left\{\frac{n.n+1.n+2\ldots n+x}{n+s}\,\frac{(-)^s}{1.2\ldots s.1.2\ldots x-s}\,R^s\right\},$$

or, as this may be written,

$$R^{-n}=\frac{[x+n]}{[n-1]}\,\Sigma\left\{\frac{(-)^s}{[s]\,[x-s]\,(n+s)}\,R^s\right\}$$

or substituting for s the values $0, 1, 2, \ldots x$, the formula is

$$R^{-n}=\frac{[x+n]}{[n-1]}\left\{\frac{1}{[0]\,[x]\,n}R^0-\frac{1}{[1]\,[x-1]\,(n+1)}R^1+\frac{1}{[2]\,[x-2]\,(n+2)}R^2-\ldots\right\}$$

continued up to the term involving R^x, which is the theorem in question.

XIX. *On the Thermal Effects of Fluids in Motion.*—Part III. *On the Changes of Temperature experienced by bodies moving through Air.* *By Professor* W. THOMSON, *A.M., LL.D., F.R.S. &c., and* J. P. JOULE, *LL.D., F.R.S. &c.*

Received June 21,—Read June 21, 1860.

THIS interesting branch of our researches has been prosecuted by us from time to time since 1856. In the spring of that year we commenced our experiments by trying the effect of whirling thermometers in the air. This process had been confidently recommended as a means of obtaining the temperature of the atmosphere, but we were sure that the plan was not absolutely correct, and one of us had, as early as 1847, explained the phenomena of "shooting stars" by the heat developed by bodies rushing into our atmosphere. In our early experiments we whirled a thermometer by means of a string, alternately quickly and slowly, and it was found that the thermometer was invariably higher after quick than after slow whirling, in some cases the difference amounting to as much as a degree FAHRENHEIT. We also succeeded in exhibiting the same phenomenon by whirling a thermo-electric junction. In 1857 we resumed the subject, using an apparatus consisting of a wheel worked by hand, communicating rapid rotation to an axle, at the extremity of which an arm carrying a thermometer, with its bulb outwards, was fixed. The distance between the centre of the axle and the thermometer bulb was 39 inches. The thermometers made use of were filled with ether or chloroform, and had, the smaller 275, and the larger 330 divisions to the degree C. The lengths of the cylindrical bulbs were $\frac{9}{10}$ and $1\frac{4}{10}$ inch, their diameters ·26 and ·48 of an inch respectively. The method of experimenting was to revolve the thermometer bulb at a certain velocity until we knew by experience that it had obtained the full thermal effect, then to stop it as suddenly as possible and observe the temperature.

Alternately with these observations others were made to ascertain the temperature after a slow velocity, the effect due to which was calculated from the other observations, on the hypothesis that it varied with the square of the velocity. In all cases the results in the Tables are means of several experiments.

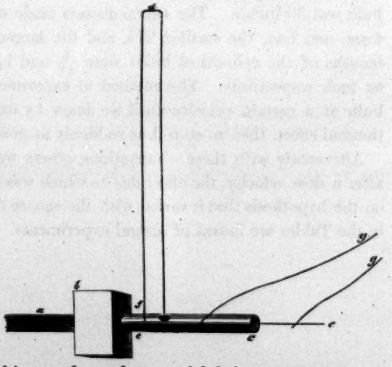
SERIES I.—Bulb ·26 inch diameter.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.
46·9 and 24	0·082	0·018	0·1	148·8
51·5 and 24	0·098	0·018	0·116	151·2
68·1 and 24	0·151	0·018	0·169	165·6
72·7 and 24	0·191	0·018	0·209	159
78·7 and 24	0·228	0·018	0·246	158·6
84·8 and 24	0·251	0·018	0·269	163·5
103·7 and 24	0·333	0·018	0·351	175
130·2 and 24	0·531	0·018	0·549	175·7
133·2 and 24	0·607	0·018	0·625	168·5
145·4 and 24	0·676	0·018	0·694	174·6

SERIES II.—Bulb ·48 inch diameter.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.
36·3 and 18	0·039	0·015	0·054	156·2
66·6 and 18	0·112	0·015	0·127	186·9
84·8 and 18	0·158	0·015	0·173	203·9
125·6 and 18	0·427	0·015	0·442	189

In the following experiments, made in the spring of 1859, thermo-electric junctions of copper and iron wire were whirled, and the effect measured by a THOMSON'S reflecting galvanometer. The arrangement will be understood from the adjoining sketch, where



a is the axle of the whirling apparatus. b a block of wood placed on the end of the axle; to this is attached $c\,c'$, a copper tube, $\frac{3}{16}$ths of an inch in diameter, with a hole in its side. $d\,e$ is a copper wire, which, entering the hole passes along the axis of the tube, from which it is insulated by non-conducting material. $d\,f$ is an iron wire soldered at d to the copper wire. $g\,g$ are thick copper wires, communicating at their remote ends with the galvanometer. They apply to the tube and wire with a springing force, perfect contact being maintained by keeping the touching surfaces clean, and lubricated with oil. A thin piece of wood, not drawn in the sketch, was attached to the block of wood. It was made to extend to within 1, 2, or 3 feet off d, according as the velocity was to be

slow or quick. The wires being tied to it, were prevented from twisting out of their proper position. The distance of d from the axis of revolution was generally 44 inches. The thermal value of the indications of the galvanometer was repeatedly ascertained by direct observations of the effect of heating the junctions.

The following Tables comprise the results of those experiments in which the junction was placed at right angles to the direction of its motion.

SERIES III.—Junction of wires $\frac{1}{100}$th of an inch in diameter.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.
53·6 and 21	0·21	0·037	0·247	108
77·8 and 17·5	0·258	0·025	0·283	146·3
105 and 18	0·373	0·026	0·399	166·2
126·4 and 44·8	0·320	0·058	0·378	205·6
146 and 25	0·673	0·030	0·703	174·1
159·3 and 34	0·866	0·041	0·907	167·3
180 and 48	0·671	0·051	0·722	211
186·6 and 48·3	0·967	0·071	1·038	181·3
221 and 47	1·393	0·050	1·443	184
300·5 and 105·8	2·364	0·333	2·697	183
315·6 and 73	3·572	0·202	3·774	162·5
326·5 and 66·2	4·133	0·172	4·305	157·3
372·5 and 66·4	5·21	0·170	5·380	160·6

SERIES IV.—Junction of wires $\frac{1}{40}$th of an inch in diameter.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.
29 and 17·5	0·022	0·012	0·034	157·2
46·2 and 15·5	0·157	0·026	0·183	108
73·7 and 16·75	0·281	0·024	0·305	133·5
90 and 17	0·363	0·013	0·376	146·8
139·1 and 26	0·61	0·021	0·631	175·1
155·6 and 26	0·878	0·024	0·902	163·9
246·4 and 31	1·482	0·023	1·505	200·8
262·6 and 35	2·087	0·045	2·132	179·8

SERIES V.—Junction of wires $\frac{1}{17·5}$th of an inch in diameter.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.
64·03 and 33·96	0·127	0·049	0·176	152·6
91·48 and 41·17	0·204	0·073	0·277	173·8
134·9 and 51	0·67	0·112	0·782	152·5
160·73 and 47·34	0·685	0·097	0·782	181·8
177·9 and 48·25	0·863	0·100	0·963	181·3
208 and 44	1·469	0·071	1·540	168

SERIES VI.—Junction of wires $\frac{1}{87}$th of an inch in diameter.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.
93·1 and 39	0°·198	0°·042	0°·240	190
109·6 and 52·4	0·239	0·072	0·311	196·5
133·96 and 58·3	0·432	0·100	0·532	183
163·7 and 55·2	0·654	0·084	0·738	190·5

From the above Tables it is manifest that the thermal effect increases nearly with the square of the velocity; it is, however, a little greater at low velocities than accords with this law. Taking, therefore, the means of the foregoing results, and rejecting all those obtained from a velocity under 100 feet per second, we obtain the following summary:—

Material of the whirled cylinder.	Diameter.	Velocity due to 1° Cent.
Glass	0·26	173·45
Glass	0·48	189
Copper-iron . . .	0·01	177·54
Copper-iron . . .	0·025	179·9
Copper-iron . . .	0·057	170·9
Copper-iron . . .	0·115	190
Mean		180·13

It may be inferred from the above that the thermal effect is independent of the kind of material whirled, provided its surface is smooth; and that it is likewise independent of the diameter of the cylinder moving in a direction perpendicular to its length.

In the next experiments we whirled the junctions parallel to the direction of motion.

SERIES VII.

Diameter of wire.	Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.	Means.
·01	123·4 and 45·2	0°·415	0°·064	0°·479	178·3	172·1
	186·7 and 54·2	1·160	0·107	1·267	165·9	
·057	126·5 and 39·6	0·59	0·058	0·648	157·1	160·55
	206·6 and 44	1·518	0·072	1·59	164	
·115	100·5 and 44·8	0·215	0·053	0·268	194·1	182·7
	182·7 and 50	1·053	0·085	1·138	171·3	

The general mean of the velocities due to 1° Cent. is therefore 171·78, which is not notably different from the result obtained when the wire was placed at right angles to the direction of motion. The absence of any considerable effect arising from the shape of the body whirled, was also shown by the following results obtained with a junction of flattened wires a quarter of an inch broad and one-thirtieth of an inch thick.

SERIES VIII.

Position of junction.	Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.	Mean.
Flat side against the air	85·8 and 40	0°·165	0°·046	0°·211	186·6	180·6
	156·5 and 52	0·683	0·085	0·768	178·6	
	164·4 and 48	0·736	0·074	0·810	182·6	
Thin edge against the air	182·4 and 54·3	0·811	0·074	0·885	193·9	

The general mean of all the foregoing results is 179·15 feet per 1° Cent. The phenomena hitherto observed seemed to point to the effect of stopping air as a cause, since 145 feet per second is the velocity of air equivalent to the quantity of heat required to raise its substance, under constant pressure, by 1° Cent. temperature; and it was reasonable to infer that a portion of the effect was lost by radiation. The following experiments, made with a junction of fine wires covered loosely with cotton-wool or tow, enabled us to eliminate all effects but those due to stopped air. Their results will be found to agree closely with theory.

SERIES IX.

Position of junction.	Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C.	Mean.
Cotton-wool closely tied about the junction of fine wires	91·3 and 34	0°·25	0°·04	0°·29	169·6	148·76
	112 and 26	0·447	0·025	0·472	162·8	
	135·8 and 40·6	1·37	0·14	1·51	110·5	
	140·3 and 24	0·823	0·024	0·847	152·4	
	167·6 and 43·5	1·188	0·085	1·273	148·5	
Junction of fine wires placed in a small wicker basket filled with cotton-wool or tow	94·1 and 35	0·494	0·079	0·573	124	144·53
	95·7 and 25·3	0·426	0·032	0·458	141·1	
	105·5 and 27·6	0·33	0·026	0·356	168·3	
	113·5 and 33	0·409	0·038	0·447	169·5	
	116·8 and 33	0·639	0·055	0·694	140·1	
	116·8 and 47·4	0·739	0·145	0·884	124·2	

When the junction was placed in the basket, without any cotton-wool or tow, a velocity of 160·1 ft. per second was required to give 1°. N.B. The basket was so open that its orifices amounted to half the entire area.

In several of our experiments with very slow velocities there appeared to be a greater evolution of heat than could be due to the stopping of air. This circumstance induced us to try various modifications of the surface of the whirled body. In the first instance we covered the bulb of the thermometer used in the second series of experiments with five folds of writing-paper, and then obtained the following results:—

SERIES X.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C., or V_{1°, on the hypothesis that $V_{1^\circ} = \frac{v}{\sqrt{t}}$.
36·3 and 18	0·045	0·015	0·060	148·2
51·5 and 18	0·115	0·015	0·130	142·8
72·6 and 18	0·146	0·015	0·161	180·9
118 and 18	0·385	0·015	0·400	186·6

It will be seen from the last column that the effect at slow velocities was greater than that which might have been anticipated. We were thus led to try the effect of a further increase of what we may call "fluid friction." In the next series the bulb was wrapped with fine iron wire.

SERIES XI.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C., or V_{1°, on the hypothesis that $V_{1^\circ} = \frac{v}{\sqrt{t}}$.
15·36 and 7·68	0·022	0·008	0·030	88·8
23·04 and 15·36	0·069	0·03	0·099	73·2
30·71 and 15·36	0·118	0·03	0·148	79·8
46·08 and 15·36	0·177	0·03	0·207	101·3
69·12 and 15·36	0·267	0·03	0·297	126·8
111·34 and 15·36	0·530	0·03	0·560	148·8
126·72 and 15·36	0·598	0·03	0·628	160
153·55 and 15·36	0·850+	0·03	0·880+	163.4—

In the next experiments the bulb was wrapped with a spiral of fine brass wire.

SERIES XII.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C., or V_{1°, on the hypothesis that $V_{1^\circ} = \frac{v}{\sqrt{t}}$.
7·68 and 1·92	0·006	0·002	0·008	86·3
15·36 and 7·68	0·033	0·008	0·041	75·8
23·04 and 15·36	0·070	0·041	0·111	69·1
30·71 and 15·36	0·105	0·041	0·146	80·3
46·08 and 19·2	0·120	0·075	0·195	104·4
76·8 and 23·04	0·203	0·111	0·314	137·1
115·18 and 23·04	0·570	0·111	0·681	139·5
148·78 and 76·8	0·488	0·314	0·802	166·2

The last columns of the above Tables clearly indicate that at slow velocities a source

of heat exists besides that from stopped air. It is also evident that, as the velocity increases, this thermal cause decreases; for at a velocity of 150 feet per second the thermal effect is such as would be due to the influence of stopped air alone.

In prosecuting still further this part of our subject we made the following arrangement. A disc of mill-board, 32 inches in diameter, was fixed to the end of the axis of the whirling apparatus. An ether thermometer, whose bulb was one-fourth of an inch in diameter, was tied by its stem to the face of the disc, so that the bulb was 15 inches distant from the axis of revolution, and 1 inch from the margin of the disc. In the following Table the first five experiments were made with the above arrangement, but in the last two a thermo-electric junction of thin copper and iron wires, tied closely to the mill-board, was substituted for the ether thermometer.

SERIES XIII.

Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C., or V_{1°, on the hypothesis that $V_{1^\circ} = \frac{v}{\sqrt{t}}$
3·15 and ·5	0·029	0·005	0·034	17·1
7·85 and 3·15	0·027	0·034	0·061	31·7
15·7 and 7·85	0·052	0·061	0·113	46·6
31·4 and 15·7	0·022	0·113	0·135	85·5
Thermo-electric junction 63·3 and 27·4	0·106	0·120	0·226	133·3
Thermo-electric junction 90·2 and 25	0·286	0·116	0·402	142·3

The surface of the mill-board disc being rather rough, it was judged desirable to make similar experiments with a disc of sheet zinc. This was perfectly smooth, 36½ inches in diameter. The thermometer bulb was fixed at 17·1 inches distance from the axis.

SERIES XIV.

Velocities in the alternate experiments in feet per second.	Difference of thermal effect.	Estimated effect of low velocity.	Thermal effect of high velocity.	Velocity due to 1° C., or V_{1°, on the hypothesis that $V_{1^\circ} = \frac{v}{\sqrt{t}}$
1·71 and ·57	0·024	0·010	0·034	9·2
3·42 and 1·71	0·017	0·034	0·051	15·1
8·55 and 3·42	0·027	0·051	0·078	30·7
17·1 and 8·55	0·023	0·078	0·101	53·8
34·2 and 17·1	0·046	0·102	0·148	88·8
57·28 and 17·1	0·070	0·102	0·172	138·3

The last columns of the two foregoing Tables clearly show the inapplicability of the law of the increase of temperature with the square of the velocity, at low velocities. The thermal effect appears even to increase at a slower rate than simply with the velocity. This phenomenon may, we think, be ascribed to the internal fluid friction of the particles

of air among themselves, which Professor STOKES has proved to exist, by his researches on the motion of pendulums. We may easily apprehend that in such experiments as our last, the entire face of the disc is covered with a film of air, which revolves along with it at very slow velocities. As the velocity increases there will still be a film of air adhering to the disc, but with the difference that it will be constantly replaced by fresh stopped air, the thermal effect of which will ultimately be the only recognizable phenomenon.

A very interesting and important branch of our subject was to inquire into the thermal phenomena which take place at the surface of a sphere passing rapidly through air. Some of our experiments on this subject have been made by blowing air from a large bellows against a ball; others by whirling a ball or sphere in the air by means of the apparatus already described. We shall commence by describing the latter, in some of which a thermo-electric junction was employed, and in others an ether thermometer.

SERIES XV.—Wooden ball 2 inches in diameter, with a thermo-electric junction of fine copper and iron wires made even with the surface.

Position of the junction in respect to the direction of motion.	Velocities in alternate experiments.	Difference of thermal effect.
		°
In front, or anterior	75·6 and 23·1	0·269
	118·4 and 23·1	0·517
	141·5 and 39·5	0·745
At the side, or equatorial...	74 and 28·5	−0·146
	115 and 26·3	0·283
	120 and 40	0·020
In the rear, or posterior ...	71·5 and 25	0·093
	112·4 and 19·3	0·414
	113·7 and 42	0·280

In the above experiments differential results for the several pairs of velocities are alone given, so that, although one of the quantities has a negative sign, there is no proof of actual cooling effect. In the next experiments we whirled a thin glass globe, 3·58 inches in diameter, placed at a distance of 38 inches from the axle of the apparatus. The small bulb of an ether thermometer was kept in contact with the glass.

Series XVI.

Position of the bulb of the thermometer in respect to the direction of motion.	Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Thermal effect due to low velocity.	Thermal effect due to high velocity.
In front of the globe	3·84 and 1·92	0°·002	0°·001	0°·003
	7·68 and 3·84	0·007	0·003	0·010
	15·36 and 7·68	0·143	0·010	0·153
	23·04 and 15·36	0·106	0·153	0·259
	38·4 and 15·36	0·133	0·153	0·286
	57·5 and 15·36	0·211	0·153	0·364
At the side of the globe ...	3·84 and 1·92	0·029	0·007	0·036
	7·68 and 3·84	0·109	0·036	0·145
	15·36 and 7·68	0·138	0·145	0·283
	23·04 and 7·68	0·181	0·145	0·326
	38·4 and 23·04	0·000	0·326	0·326
	57·5 and 23·04	0·087	0·326	0·413
In the rear of the globe ...	3·84 and 1·92	0·011	0·004	0·015
	7·68 and 3·84	0·024	0·015	0·039
	15·36 and 7·68	0·147	0·039	0·186
	23·04 and 15·36	0·076	0·186	0·262
	38·4 and 15·36	0·062	0·186	0·248
	57·5 and 15·36	0·091	0·186	0·277
	70·92 and 15·36	0·204	0·186	0·390

In the next experiments, a 12-inch globe, such as is used in schools, was fixed at a distance of 3 feet from the axis of the revolving apparatus. The ether thermometer was generally employed, as in the last series, but for the highest velocity a thermo-electric junction of thin wires placed close to the globe registered the thermal effect.

Series XVII.

Measurer of heat, and its position in respect to the direction of the motion.	Velocities in the alternate experiments, in feet per second.	Difference of thermal effect.	Thermal effect due to low velocity.	Thermal effect due to high velocity.
Anterior. Ether thermometer ...	3·72 and 1·24	0°·019	0°·009 estim^{d}.	0°·028
	7·44 and 3·72	0·008	0·028	0·036
	14·88 and 7·44	0·028	0·036	0·064
Anterior. Thermo-electric junction	39·68 and 7·44	0·200	0·036	0·236
Equatorial. Ether thermometer ...	3·72 and 1·24	0·007	0·003 estim^{d}.	0·010
	7·44 and 3·72	0·013	0·010	0·023
	14·88 and 7·44	0·024	0·023	0·047
Equatorial. Thermo-electric junction	39·37 and 7·44	0·170	0·023	0·193
Posterior. Ether thermometer ...	3·72 and 1·24	0·024	0·012 estim^{d}.	0·036
	7·44 and 3·72	0·022	0·036	0·058
	14·88 and 7·44	0·046	0·058	0·104
Posterior. Thermo-electric junction	37·2 and 7·44	0·140	0·058	0·198

In the experiments in which air was blown against a sphere, we made use of a large organ-bellows, from which a constant stream of air could be kept up at velocities dependent upon the weights laid on. In our first trials, the air issued from a circular

aperture $2\frac{1}{2}$ inches in diameter, and the ball was placed, at half an inch distance, in front of the aperture. We shall, as before, call that point of the ball which was nearest the wind, the Anterior Pole; the most sheltered point, the Posterior Pole; and the intermediate part, the Equator. The balls were furnished with thermo-electric junctions of thin copper and iron wires, made flat with the surface, the junctions being in each case 90° apart from one another.

Series XVIII.—½-inch Wooden Ball.

Velocity of air.
68 ft. per sec. ... Equator 0°·114 colder than Anterior Pole ... Posterior Pole 0°·067 colder than Equator.

Series XIX.—1-inch Wooden Ball.

Velocity of air.
1·2 ... Equator 0°·088 warmer than Anterior Pole.
3·6 ... Equator 0·129 warmer than Anterior Pole ... Posterior Pole 0°·03 warmer than Equator.
7·2 ... Equator 0·160 warmer than Anterior Pole ... Posterior Pole 0·022 warmer than Equator.
14·4 ... Equator 0·120 warmer than Anterior Pole ... Posterior Pole 0·018 colder than Equator.
28·8 ... Equator 0·056 warmer than Anterior Pole ... Posterior Pole 0·018 colder than Equator.
36 ... Equator 0·008 colder than Anterior Pole.
48 ... Equator 0·035 colder than Anterior Pole.
57·6 ... Equator 0·056 colder than Anterior Pole..... Posterior Pole 0·090 colder than Equator.
73 ... Equator 0·245 colder than Anterior Pole.
105 ... Equator 0·380 colder than Anterior Pole..... Posterior Pole 0·232 colder than Equator.

In our next series, one junction was placed within the bellows, and the other in contact with the different parts of the 1-inch ball. All the results will be seen to indicate, as might have been anticipated, that the junction within the bellows was warmer than any part of the ball.

Series XX.

Velocity of air.	Pressure of air in the bellows, in inches of water.	Cold of Anterior Pole, in respect to the inner junction.	Cold of Equator, in respect to the inner junction.	Cold of Posterior Pole, in respect to the inner junction.
2·4	0·003 estimated	0°·098	0°·065	0°·028
3·6	0·006 estimated	0·094	0·065	0·028
7·2	0·025 estimated	0·083	0·103	0·060
14·4	0·105 estimated	0·110	0·089	0·109
28·8	0·42 estimated	0·102	.....	0·112
73	2·7 estimated	0·188	0·309	0·300
105	5·6 measured	0·195	.....	0·360

A further modification of the experiments was made by placing a glass tube 3 feet long and of $1\frac{1}{4}$-inch interior diameter, within the aperture, so that two-thirds of the tube was inside, and one-third outside of the bellows. A ball furnished with junctions 90° distant from each other was placed within the tube.

Series XXI.—Wooden Ball, 1 inch diameter.

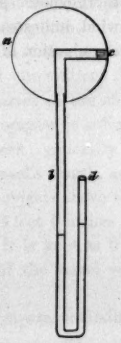
Velocity of air.		
1·8	Equator 0°·045 warmer than Anterior Pole	Posterior Pole 0°·052 warmer than Equator.
2·7	Equator 0·056 warmer than Anterior Pole	Posterior Pole 0·052 warmer than Equator.
5·4	Equator 0·074 warmer than Anterior Pole	Posterior Pole 0·035 warmer than Equator.
10·8	Equator 0·052 warmer than Anterior Pole	Posterior Pole 0·017 warmer than Equator.
21·6	Equator 0·037 warmer than Anterior Pole	Posterior Pole 0·008 colder than Equator.
43·2	Equator 0·011 warmer than Anterior Pole	Posterior Pole 0·013 colder than Equator.
54	Equator 0·019 colder than Anterior Pole	Posterior Pole 0·014 colder than Equator.
62		Posterior Pole 0·023 colder than Equator.
83·8		Posterior Pole 0·041 colder than Equator.
108	Equator 0·091 colder than Anterior Pole	Posterior Pole 0·086 colder than Equator.

Series XXII.—Wooden Ball, ½ inch diameter.

Velocity of air.		
1·8	Equator 0°·048 warmer than Anterior Pole	Posterior Pole 0°·050 warmer than Equator.
5·4	Equator 0·030 warmer than Anterior Pole	Posterior Pole 0·047 warmer than Equator.
10·8	Equator 0·023 warmer than Anterior Pole	Posterior Pole 0·031 warmer than Equator.
21·6	Equator 0·008 warmer than Anterior Pole	Posterior Pole 0·012 warmer than Equator.
43·2	Equator 0·006 colder than Anterior Pole	Posterior Pole 0·009 warmer than Equator.
54	Equator 0·019 colder than Anterior Pole	Posterior Pole 0·006 colder than Equator.
62	Equator 0·026 colder than Anterior Pole	Posterior Pole 0·014 colder than Equator.
83·8	Equator 0·040 colder than Anterior Pole	Posterior Pole 0·031 colder than Equator.
108	Equator 0·068 colder than Anterior Pole	Posterior Pole 0·050 colder than Equator.

The general result is that at slow velocities of air there is a gradual increase of temperature from the anterior to the posterior pole, but the reverse at high velocities. We observed a great effect for slow velocities at the commencement of an experiment, which gradually declined on continued blowing. This phenomenon was apparently owing to circumstances in connexion with the temperature of the orifice and of the bellows.

The causes of the thermal effects on the surface of balls slowly passing through air are very complicated, as they arise from the effects of stopped air, fluid friction, and varied pressures. In order, if possible, to throw some light on these, we made the following observations:—



1st. That when the 12-inch globe passed through the air at the velocity of about 12 feet per second or under, the air at the equatorial part moved in the reverse direction. We did not observe the velocity, if it existed, at which this phenomenon ceased to take place*.

2nd. An ivory ball, 1·7 inch diameter, had holes drilled from points of the surface 90° asunder, which holes met at the centre of the ball. Into the lower one (see adjoining figure) a bent glass tube, partly filled with water, was cemented; in the other, at *c*, a porous wooden plug was placed. It was then found that when *c* was made the anterior pole in a blast from the bellows, a pressure was experienced able to

* See 'Proceedings of the Royal Society,' June 18, 1857, p. 558.

produce a difference of level in the tubes *b* and *d* equal to 2·5 inches. When *c* was put in the equatorial position, there was, on the contrary, a suction equal to 1·2 inch. When *c* was made the posterior pole there was also a suction, equal, however, to only 0·1 inch. Having tied a thick fold of silk over the orifice *d*, we tried the same thing in a strong breeze of wind, when we found that on making *c* the anterior pole, we had a pressure amounting to 0·6 of an inch; on making *c* equatorial, a suction of 0·3; and on making *c* the posterior pole, a suction of 0·05 inch.

We have not hitherto been able to detect any change in the thermal effect, owing to the whistling sound of wire or other bodies rapidly whirled. We think it possible that this vibratory action decreases the resistance and the evolution of heat. Some of the sounds produced are interesting and worthy of further investigation. When a small piece of paper was attached to the revolving wire, we obtained a continuous succession of loud cracks similar to those of a whip.

But although this and other parts of our subject remain to be cleared up, we believe that it will be found that at all high velocities the thermal effect arises entirely from stopped air, and thus is independent of the shape and mass of the body, and of the temperature and density of the atmosphere. From some experiments described in the 'Proceedings of the Royal Society' of June 19, 1856, p. 183, we inferred that a body placed in a stream of air moving with a velocity of 1780 feet per second, was raised 137° C. above the temperature of that stream. This gives 152 feet per second as the velocity due to 1°, while our direct results, given in the present paper, indicate 179.

It must be obvious that a thermometer placed in the wind registers the temperature of the air, plus the greater portion, but not the whole, of the temperature due to the *vis viva* of its motion. In a place perfectly sheltered from the wind, the temperature of a thermometer immersed in the air will be that of the wind, plus the whole temperature due to the *vis viva* of the moving air. In accordance with this we have found that a thermometer placed in a sheltered situation, such as on the top of a wall opposite the wind, indicates a higher temperature than when it is exposed to the blast. A minute examination of these phenomena cannot fail to interest the meteorologist.

XX. *Reduction and Discussion of the Deviations of the Compass observed on board of all the Iron-built Ships, and a selection of the Wood-built Steam-ships in Her Majesty's Navy, and the Iron Steam-ship 'Great Eastern'; being a Report to the Hydrographer of the Admiralty.* By Frederick J. Evans, *Esq., Master R.N., Superintendent of the Compass Department of Her Majesty's Navy. Communicated by Captain* Washington, *R.N., F.R.S., by command of the Lords Commissioners of the Admiralty.*

Received May 5,—Read June 21, 1860.

Sir, London, April 18, 1860.

In compliance with the general instructions I received from you on my appointment, to observe carefully the working of the Mariner's Compass in the ships of Her Majesty's Navy, and especially in iron vessels, both for the security of their navigation and the aid of science, I now beg leave to submit for your consideration the following Report treating on these points, and in which is embodied an analysis of the magnetic character of all the iron-built ships in Her Majesty's Navy, as also of several of the wood-built steam-ships.

In directing attention to this analysis, as given in a series of Tables, it is necessary to advert to the observations on which it is based, as resulting from a general system pursued in the Royal Navy.

On the foundation of the Compass Department in 1843, a periodical examination of the disturbance caused by the iron on the compass in each ship,—or the deviation of the compass as it is now familiarly known to seamen,—was directed to be made by the Lords Commissioners of the Admiralty; the records of this examination are duly preserved in the Hydrographic Office, and have been employed in this investigation.

The compass specially selected at this period (and since retained with a few modifications) for the navigation of Her Majesty's ships, and with which all observations for the deviation are made, and to which the steering or binnacle compasses of the ship are referred, is well known as the "Admiralty Standard*." This compass is solidly fixed in the middle line of the ship, within the limits of the quarter-deck; generally at a distance from the stern varying from one-fifth to one-tenth of the vessel's length, and raised sufficiently high from the deck to secure bearings of terrestrial objects above the gunwales or bulwarks, which ensures a height varying from about 4 feet 6 inches to 6 feet 6 inches; an essential condition of its arrangement being that it is kept as free from the immediate vicinity of iron as the nature and equipment of the vessel will permit.

The details of all the essential parts of the Admiralty Standard compass, including

* A brief description of this compass, and the chief points in its construction, is appended.

the cards and needles, are uniform throughout; the intensities of the latter being remarkably so, and also permanent over long periods of time: the observations made with this compass are therefore strictly comparable, and it will be understood that the results given in this Report, except when specified to the contrary, and the inferences arising therefrom, must be considered as applying to a compass in the various details of position and structure just described.

The analysis of the deviations of the compass in iron-built vessels, embraces forty-two ships of the Royal Navy; and including the wood-built screw and paddle-wheel steam-vessels, as also the deviations observed in various parts of the steam ship 'Great Eastern' during her experimental trip to Portland in the autumn of 1859, has involved a computation of nearly two hundred and fifty Tables.

In order to render the analysis complete as a standard of reference, there is appended certain statistical information relating to each vessel, including tonnage, and exact position and height of standard compass: these details will be found necessary in a critical examination of the magnetic characteristics of ships in general.

In the analysis of the Deviation Tables, I have employed Mr. Archibald Smith's formula for computing the magnetic coefficients, as deduced from Poisson's General Equations given in the Supplement to the "Practical Rules for ascertaining and applying the Deviations of the Compass caused by the Iron in a Ship," furnished to Her Majesty's Ships; and also in the Philosophical Transactions for 1846.

In this formula the deviation (δ) of the compass on board ship, reckoned positive when the north point of the needle deviates to the east, is given by the following expression:—

$$\delta = A + B \sin \zeta' + C \cos \zeta' + D \sin 2\zeta' + E \cos 2\zeta',$$

A, D, E being constants depending only on the amount, quality, and arrangement or position of the iron in the ship; B and C depending on these, and also on the magnetic dip and horizontal intensity; and ζ' the azimuth (by disturbed compass) of the ship's head, reckoned from the magnetic north to the east.

This formula is only approximate; but is sufficiently correct when the deviation does not exceed about 20°. The accurate formula involves calculations too laborious to be applied to ordinary cases.

Without entering on the nature and action of the magnetic forces which cause the deviation of the compass on board ship,—to be found in the works to which I have alluded, as also in the introduction to Dr. Scoresby's late Voyage round the World for magnetical research, edited by Mr. Archibald Smith,—further than to attach a physical meaning to the coefficients for practical elucidation, it is necessary to premise that the investigations of the Astronomer Royal* are in accord with the general terms

* "Account of Experiments on Iron-built ships, instituted for the purpose of discovering a correction for the deviation of the Compass produced by the Iron of the ships," Philosophical Transactions, Part I. 1839. "Discussion of the observed Deviations of the Compass in several ships, Wood-built and Iron-built: with a General Table for facilitating the examination of Compass Deviations," by G. B. Airy, Esq., Astronomer Royal, Philosophical Transactions for 1856.

of this formula; observing, that in those investigations the coefficients A and E are eliminated by the assumption that the soft iron is symmetrically distributed on each side of the fore-and-aft line of the ship.

The meaning of the several coefficients is as follows:—

A is a constant deviation, real or apparent; + if easterly deviation is in excess, — if westerly; when real, it arises from the induction of the horizontal force of the earth on masses of soft iron unsymmetrically distributed; when only apparent, as in nearly every case recorded, it is considered due to prism, or index error of the compass on board, or of the compass employed on shore in obtaining reciprocal bearings, as also local disturbance of the latter; and, when the deviation has been observed by the bearing of a distant object, that the latter has been imperfectly determined.

B and C are due to the combined effects of the permanent magnetism of the hard iron; the deviation produced by which varies inversely as the horizontal force at the place, and that induced by the vertical part of the earth's force on the soft iron in the ship, the deviation produced by which varies as the tangent of the dip. This deviation has been termed "polar-magnet" by the Astronomer Royal, and "semicircular" by Mr. A. Smith, from the nature and appearance of the curve when graphically delineated.

B represents that part of the combined attraction acting in a fore-and-aft direction; + if before the compass, — if abaft it; that is, the north end of the needle is attracted to the bow in the former case, and to the stern in the latter.

C is that portion of the combined attraction acting in an athwart-ship direction; + if the north end of the needle is drawn to the starboard side, — if drawn to the port side of the ship.

D and E, known as the permanent coefficients, from their (theoretically considered) unchanging value in all magnetic latitudes, are due to the horizontal induction of the soft iron in the ship, and produce a "quadrantal" deviation; the term multiplied by D having its four maxima at the intercardinal points, and that by E at the cardinal points.

The values of D are considered by theory to arise from masses acting in a fore-and-aft, or transverse direction; + from those before or abaft, — from those on either side.

E is in general so small as to be practically unimportant.

Tables of Magnetic Elements of various Ships in Her Majesty's Navy, Iron and Wood-built.

The results of the analysis of the Tables of Compass Deviation are thus arranged:—

Table I. The iron-built vessels arranged according to tonnage: this analysis includes every Deviation Table of such vessels recorded in the Admiralty.

Table II. includes the floating batteries; one iron-built, and the others wood-built plated with iron.

Table III. A selection from the wood-built screw steam-vessels, embracing those of large, medium, and small dimensions.

Table IV. A selection from the wood-built paddle-wheel steam-vessels, embracing vessels of various dimensions.

The selected examples of Tables II. and III. must be understood as adopted to represent the general types of their classes: the examples in these Tables, of deviations observed on Foreign stations, are selected from the evident skill and care that has been bestowed on the observations, and from their perfect illustration of the general nature of the magnetic change in wood-built steam-ships.

Table V. The magnetic coefficients of the steam-ship Great Eastern, as observed in various parts of the vessel by myself, conjointly with Mr. RUNDELL, the Secretary to the Liverpool Compass Committee.

The general tabular arrangement it is considered requires little further explanation than the titles of the various columns convey. The column "Ship's force to head" is the natural sine of the corresponding value of the coefficient B, and is in fact the proportion of the ship's force to head, to the earth's horizontal force. The column "Ship's force to starboard" is the natural sine of the corresponding value of the coefficient C, and is the proportion of the ship's force to the starboard side, to the earth's horizontal force.

The resultant of B and C is the ship's force, and is in its direction $\left[\tan^{-1}\frac{C}{B}\right]$ and amount $[\sqrt{B^2+C^2}]$ the equivalent of the "true starboard angle" (measured from the bow round by the starboard side to the bow again), or "neutral position;" and of the "modulus" of polar-magnet deviation in Mr. AIRY's paper in the Philosophical Transactions for 1856.

It will be observed that in the results obtained from Deviations observed on Foreign stations (noted in *italics*), the total force of the ship is given in two lines, the upper line being the proportion of the ship's force to the horizontal force of the earth at the place, the lower line being the proportion of the ship's force to the horizontal force in England, so as to allow a comparison to be made of the absolute force of the ship at various stations.

For convenience, 1·000 has been adopted to represent the value of the earth's horizontal magnetic force at the several English ports where Her Majesty's ships are usually swung, viz. Greenhithe, Sheerness, Portsmouth, and Plymouth: for other stations I have adopted those given by Mr. AIRY in the paper of 1855 alluded to; and for several places not included in his discussion, reference has been made to the chart of Absolute Magnetic Intensity by General SABINE*, employing for the reduction to the horizontal component, the most recent determinations of the magnetic dip with which I am acquainted.

A comparative Table of the foregoing elements, with the horizontal force as given by GAUSS in his 'Atlas des Erdmagnetismus,' reduced to the same unit of measure, is appended, as being probably of use in any future inquiry or discussion.

I now proceed to direct attention to various features exhibited in the several Tables,

* KEITH JOHNSON'S 'Physical Atlas,' 2nd edition.

and shall venture to suggest what would appear from fair inferences to be the leading principles of the magnetism of the ships included therein, and their practical application.

It has been deemed unnecessary to introduce an analysis of the compass deviations of wood-built *sailing* vessels; as, whether as ships of war with batteries of guns, or merchant vessels carrying cargo,—always excepting iron,—their deviations are small in amount, and arising in the aggregate from induced magnetism.

An intercomparison of the magnetic coefficients of iron and wood-built steam-ships is of greater importance in the investigations of the laws affecting the former, than would at first appear: the special points elicited are—

That D, which in the iron vessel ranges in value from $+1\frac{1}{2}°$ to $+6°$ and 7° (the Liverpool Compass Committee recording even a point or 11°), seldom exceeds $+1°$ in wood screw-ships, with not unfrequently a small *minus* sign in these vessels, and $+1\frac{1}{2}°$ in the wood paddle-wheel steam-ships.

A and E appear common in character and value in all the classes of vessels enumerated.

B and C thus differ:—In the wood-built vessel (in Great Britain) B is + whenever the engines are before the compass, and C is always small in value. In the iron-built vessel, B, irrespective of the machinery, is either + or − as the ship's head while building was south or north; and C may be large in value, either + or −; B nearly vanishing as the ship's head while building deviated from the magnetic meridian and approached the east or west points of the compass*.

Taking therefore the relative tonnage, horse-power, and position of the standard compass in each class of vessel, wood and iron, a judgment can be formed of the comparative magnetic effects of the engines and boilers, apart from the hull or hammered fabric of the iron ship.

Several examples occur in the Tables; from which we may infer, (1) that in an iron vessel built in England, head *south*, the north end of the needle is drawn to the bow, or B is positive. The steam machinery has the same effect; B therefore as due to the hull, is increased in amount. (2) In an iron vessel built head to the *north*, the north end of the needle is drawn to the stern, or B is negative; the steam machinery will in this case tend to diminish the value of this coefficient; and on reference to Table I. it will be observed that, as a rule, those vessels with B positive have, taking size and other conditions of compass position into consideration, large compass deviations.

But what are the combined effects of steam machinery and hull on a great change of geographic position, or in high south magnetic latitudes? An examination of the several Tables elicits some valuable information on this important point.

* The connexion between the direction of the ship's keel and head while building as referred to the magnetic meridian, and the direction and strength of her magnetic polarity, so fully experimented on by the late Dr. Scoresby and the Liverpool Compass Committee, is, I consider, fully confirmed; and there will be added to this Report the magnetic lines of the 'Great Eastern,' as another example of this remarkable feature of an iron ship's magnetism.

Referring to the magnetic changes of the *wood-built* vessels (screw or paddle) in the progress of their respective voyages to, and in the southern hemisphere, of which there are several good continuous examples, it is evident that the coefficients B and C are dependent in their change chiefly on the alteration of the magnetic dip, and that the horizontal intensity is a minor element of disturbance; it may therefore be inferred as a general rule, that in steam machinery, permanent magnetism bears but a small proportion to inductive.

This appears sufficiently from examples in Tables III. and IV.; as also that, as in the case of wood-built sailing vessels (discussed by General SABINE in the Philosophical Transactions for 1849*), the wood steam-ship's magnetism, on rapid changes of geographic position, falls short of, or "lags behind," the amount theoretically due to changes of magnetic latitude.

The wood screw-ships Plumper and Highflyer† are instructive examples of the "lagging behind" of their magnetism; in the former case, on the ship's arrival at Vancouver Island, the semicircular deviation was much in arrear of the value due to the magnetic dip, as compared with that originally obtained in England. After an interval of sixteen months, on the ship being reswung in the same locality, which she had not quitted, the deviations exceeded the original amount observed in England, approximating to the value due to the increased magnetic dip at Vancouver Island. Similar features are exhibited in the Highflyer employed in the China seas.

We have now to consider the magnetic nature of the hull of the iron vessel combined with the steam machinery; and in stating here the fact, of the former being, in the majority of the vessels investigated, highly permanent and but slightly inductive, in contradistinction to the steam machinery, I am only anticipating what will be hereafter given in proof from examples in Table I.

The position of the standard compass with reference to the steam machinery in an iron vessel, has therefore an important bearing practically and theoretically; for if it is placed in proximity to the funnel, which may be considered as the zero or measuring point for the machinery in general, the inductive magnetism of the machinery is superadded on the subpermanent magnetism of the hull, and complicates the question apparently beyond research.

An instructive practical example of this condition is afforded in the case of the 'Vulcan' iron ship: in this vessel the steam machinery is further aft than is usual in ships either of the Navy or of the mercantile marine; and it will be observed that the standard compass is only 27 feet distant from the funnel, and is elevated on the poop-deck nearly to the level of the top of the latter. Viewing the nature of the Vulcan's hull under the conditions of permanent magnetism, the maximum deviation, or ship's force,

* Contributions to Terrestrial Magnetism, Part IX.

† Commanded respectively by Captains GEORGE H. RICHARDS and CHARLES F. SHADWELL, C.B. The labour and attention bestowed by these officers in the determination of the compass deviations of their ships, and the consequent value of the results to the practice of navigation, and the theory of a ship's magnetism, are worthy of especial record.

when at the Cape of Good Hope, should have been reduced in the inverse proportion of 1·000 to 1·174, or about one-sixth, whereas by observation it had more than doubled: the polarity of the funnel and machinery, following the changes of magnetic dip (the vessel was some months employed in high south magnetic latitudes), was reversed, and thus their force of magnetism (−B) was added to that of the hull of the ship (−B also), instead of being subtracted from it, as had been the case in England.

The Simoom, a nearly sister vessel to the Vulcan, but with +B, and also observed at the Cape of Good Hope, has the conditions reversed, the semicircular deviation being smaller than its theoretical value, for the opposite reason; viz. that the force of the machinery which had been added to that of the hull in England, changing its sign, was subtracted from it at the Cape of Good Hope.

On the Nature of the Magnetism in Iron-built Ships.

The magnetic influence of steam machinery having been reviewed, the nature of the magnetism of iron-built ships can be entered on free, to a certain extent, of conditions arising from this extraneous source of compass error, and those examples fairly eliminated where it tends to embarrass the discussion.

The investigation of the coefficient D, or the disturbance arising from the horizontal induction of the soft iron in the ship, when extended over the numerous examples recorded in Table I., offers several novel and suggestive points of inquiry: the chief characteristics are,—

1. That it has invariably a *positive* sign, causing an easterly deviation in the N.E. and S.W. quadrants, and a westerly deviation in the S.E. and N.W. quadrants.

2. That its amount does not appear to depend on the size or mass of the vessel, or direction when building, or on the iron beams.

3. That a gradual decrease in amount has occurred, when examined over a number of years, in nearly every vessel that has been reviewed.

4. That the value remains unchanged in sign and amount, on changes of geographic position, confirming theoretical deductions.

5. That a value for this coefficient, not exceeding 4°, and ranging between that amount and 2°, may be assumed to represent the average or normal amount in vessels of all sizes.

The following examples support these propositions:—

1. The value not depending on the size of the vessel.

Great Eastern, of 22,000 tons .	+4° 8′	Trident, of 850 tons	+3° 26′
Himalaya . „ 3,453 „ .	+3 18	Oberon, „ 649 „	+3 23
Assistance . „ 1,820 „ .	+3 36	Onyx, „ 292 „	+3 42

As also, that the effect of iron beams, which has been assumed as a large element of disturbance, cannot be traced.

Assistance	1820 tons, iron beams	+3° 36′
Trident	850 tons, wood beams	+3 26
Industry	638 tons, iron beams	+2 40
Oberon	649 tons, wood beams	+3 27
Bloodhound	378 tons, iron beams	+3 40
Sharpshooter	503 tons, wood beams	+4 32

To establish the effect of iron beams more fully, I carried out a series of experiments on board H.M.S. Supply; and from the results it is to be inferred that their magnetic character is identical with that of the hull of the ship; being dependent, as regards polarity and permanency of magnetism, on the direction of the ship when building, and the nature of the iron.

The uniformity of the quadrantal deviation of the compass, when placed in various positions and at different heights from the deck, is thus shown:—

In middle line of the 'Supply,' 28 feet from stern,	5 ft. 0 in.	high from deck .	+2° 38′
„ 19 „	5 2	„ . .	+2 15 +2 37
„ 12 „	3 10	„ . .	+2 55
Placed 22 feet from stern, 3 feet from middle line of deck, and	3 ft. 9 in.	high	+2 56
Placed 13 feet from stern, 8 feet from middle line of deck, 2 feet from the iron top side, and 1 foot 8 inches high			+2 13

The polar-magnet or semicircular deviation varied under these conditions from 15° to 45°.

Elevation of the compass above an ordinary height from the deck necessarily diminishes the amount of quadrantal deviation, as in mast-compasses*; but within the ordinary limits, or from 2 to 6 feet from the deck, the foregoing examples show that the value is not affected. Another example was also afforded in H.M.S. Assistance, where the raising the standard compass from 4 feet 5 inches to 6 feet 4 inches above the iron beams, which diminished the "semicircular" deviation from 17° 40′ to 15°, had no perceptible effect on the "quadrantal," the values of D being respectively +3° 35′ and +3° 36′.

		Mast-compass, 45 feet from deck.	Standard compass, 5 feet from deck.	
* Great Eastern	River Thames	+1° 32′	+4° 21′	Coefficient D.
	Portland	+1 30	+4 44	
	Holyhead	+1 0	+4 8	

H.M.S. Trident, mast-compass elevated 48 feet from the deck, D—1° 8′: this is the only example that has come under my investigation of a *minus* sign. It is the effect which would be produced if the soft iron can be considered as collected in two masses,—one near the bow, the other near the stern.

2. The gradual decrease in the value of D is well marked in those ships in which the position of the compass has remained unchanged, and direct comparison has been thus afforded.

Himalaya	. in	$4\frac{1}{2}$	years,	decrease	from	3°	51′	to 3°	18′ = 0°	33′
Urgent	. . . „	4	„	„		2	58	„ 2	12 „ 0	46
Simoom	. . „	$7\frac{3}{4}$	„	„		3	57	„ 3	25 „ 0	32
Vulcan	. . . „	$8\frac{1}{2}$	„	„		3	20	„ 2	48 „ 0	32
Birkenhead	. „	4	„	„		2	53	„ 2	12 „ 0	41
Trident	. . . „	13	„	„		4	03	„ 3	26 „ 0	37
Triton	. . . „	$9\frac{1}{2}$	„	„		4	02	„ 2	37 „ 1	25
Supply	. . . „	$5\frac{1}{4}$	„	„		3	40	„ 2	15 „ 1	25
Bloodhound	„	10	„	„		3	40	„ 2	31 „ 1	9
Jackal	. . . „	14	„	„		4	57	„ 3	01 „ 1	56
Myrmidon	. „	$9\frac{1}{4}$	„	„		3	23	„ 2	45 „ 0	38
Harpy	. . . „	14	„	„		2	54	„ 2	32 „ 0	22
Lizard	. . . „	13	„	„		3	49	„ 3	4 „ 0	45
Onyx	. . . . „	4	„	„		3	42	„ 3	26 „ 0	16
Dover	. . . „	$5\frac{1}{2}$	„	„		2	38	„ 2	23 „ 0	15

3. In assuming the normal amount of quadrantal deviation in iron steam-ships as from 2° to 4°, it will be seen, from the accompanying analysis, that thirty-four of the forty-two ships in Her Majesty's Navy, or 75 per cent., are included in this condition, thus:

Quadrantal deviation, between			1°	and	2°,	2	vessels, of 1391 and 462* tons.
„	„	„	2	„	$2\frac{1}{2}$,	1	„ 164 tons.
„	„	„	2	„	3,	11	„ 1981 to 180 tons.
„	„	„	$2\frac{1}{2}$	„	$3\frac{1}{2}$,	10	„ 1764 „ 270 tons.
„	„	„	3	„	4,	10	„ 3453 „ 292 tons.
„	„	„	$3\frac{1}{2}$	„	$4\frac{1}{2}$,	3	„ 1980 „ 503 tons.
„	„	„	3	„	5,	2	„ 440 „ 340 tons.
„	„	„	4	„	5,	1	„ 267 tons, as also Gt. Eastern.
„	„	„	6	„	7,	2	„ 1954† to 267 tons.

Two questions of import here arise:—Are the results of this analysis to be deemed conclusive? and, if so, under what conditions do large quadrantal deviations occur?

It will be remembered that the two earliest iron vessels experimented on by Mr. Airy,—the 'Rainbow' in 1838, and the 'Ironsides' in 1839,—vessels probably in those

* A sailing vessel. † A floating battery.

early days considered experimental, and built of the best material, had very small quadrantal deviations, viz. 1° and 1° 6′ respectively; indeed the Astronomer Royal experienced difficulty in tracing the effects of terrestrial induction. Bearing these facts in view, and taking further into consideration that in building Government vessels stringent conditions of contract as to soundness of material are enforced, and strict supervision exercised, it may be fairly assumed that the amount given of 2° to 4° represents the average condition of a well-built ship of the best or superior iron.

On the other hand, can the inference be drawn that an iron ship with large quadrantal deviation implies inferior material being used in her construction?

Two of the most disastrous and fatal shipwrecks on record have occurred to iron-built vessels, whose magnetic characters are perfectly known. H.M.S. Birkenhead, whose permanency of magnetism (Table I.) was especially constant, and quadrantal deviation small,—2¼°+ a short time prior to her loss,—may be considered as the type, magnetically, of a "hard" iron-built ship: the Royal Charter, with a quadrantal deviation of 6°, and whose sub-permanent magnetism fluctuated more than any vessel with whose records I am acquainted, may be considered as the type, magnetically, of a "soft" iron-built ship. It will be recollected that in the wreck of these vessels under their varied circumstances, both parted amidships; the Royal Charter so suddenly and rapidly, as to invite serious attention to various points of her construction.

It is difficult to draw any comparative conclusions from these two cases, but they are placed in juxtaposition as grounds for further inquiry as to the connexion between the amount of quadrantal deviation and the nature of the iron of the ship; and it will be remarkable and not less useful, if, in the prosecution of such inquiry, it can be established that the relative qualities of the material used in iron ship-building can be discriminated by the subtle agency of the ship's compass-needle.

On the Coefficients B *and* C *in Iron-built Ships, or that part of the Compass-disturbance arising from the permanent magnetism of "hard" iron, and that induced by the vertical part of the earth's force on the "soft" iron in the ship.*

On examination of Table I., it is at once observed that in the majority of examples therein given, a permanency of magnetism exists so little affected by changes of geographic position, as materially to confirm the views entertained by the Astronomer Royal in his earliest discussion (1838), that the effect of transient induced magnetism in iron-built ships is very small comparatively.

The absence of irregular fluctuations, and the gradual diminution of the ship's force, analogous to the gradual decrease of the quadrantal deviation, are notable features; and apparently the general permanency is but little influenced by concussions from the sea, or from the repairs in dock, which necessarily must have occurred during the several years over which the observations extend.

The gradual diminution of the ship's magnetic force is shown in the following

examples, all determined in English ports, and where it has been ascertained that, from the compass remaining in the same position, the results are comparative.

The column "semicircular" deviation has been added to show the practical disturbance on the compass at its maximum.

Year.	Ship's force. Direction.	Ship's force. Amount.	Semicircular deviation.
Himalaya.			
1855.	182°	0·275	16° 0′
1856.	182	0·243	14 5
1859.	169	0·248	14 25
Urgent.			
1855.	175	0·215	12 25
1856.	170	0·183	10 35
1857.	158	0·163	9 25
1859.	170	0·151	8 45
Simoom.			
1852.	340	0·367	21 35
1852.	340	0·367	21 35
1857.	355	0·326	19 0
1859.	4	0·316	18 30
Megæra.			
1851.	190	0·232	13 25
1852.	150	0·238	13 45
1857.	162	0·219	12 40
Birkenhead.			
1847.	205	0·264	15 15
1847.	206	0·265	15 20
1848.	206	0·260	15 5
1850.	207	0·264	15 15
1851.	206	0·267	15 30
Trident.			
1846.	3	0·345	20 10
1848.	359	0·359	21 0
1849.	360	0·316	18 36
1852.	352	0·342	20 0
1856.	351	0·376	22 5
1859.	2	0·320	18 40
Caradoc.			
1848.	199	0·230	13 20
1855.	191	0·193	11 10
Triton.			
1848.	178	0·207	11 55
1852.	198	0·142	8 10
Oberon.			
1847.	294	0·266	15 25
1851.	295	0·230	13 20
Industry.			
1854.	13°	0·247	14° 20′
1856.	13	0·256	14 50
1858.	358	0·230	13 20
1858.	354	0·182	10 30
1859.	360	0·185	10 40
Sharpshooter.			
1848.	177	0·126	7 15
1850.	180	0·105	6 5
1852.	180	0·280	16 15 *
1857.	189	0·235	13 35 *
Bloodhound.			
1845.	351	0·256	14 50
1847.	351	0·209	12 5
1851.	347	0·219	12 40
1855.	350	0·207	12 0
Jackal.			
1845.	353	0·288	16 45
1849.	344	0·266	15 25
1854.	329	0·316	18 25 *
1859.	339	0·262	15 10 *
Lizard.			
1845.	351	0·236	13 40
1853.	3	0·188	10 50
1858.	5	0·172	9 55
Firequeen.			
1847.	320	0·210	12 10
1852.	329	0·197	11 20
Fairy.			
1850.	355	0·233	13 30
1852.	357	0·202	11 40
1858.	10	0·201	11 35
Princess Alice.			
1844.	2	0·257	14 55
1850.	358	0·225	13 0
1855.	348	0·213	12 20
Torch.			
1846.	340	0·206	11 50
1852.	356	0·186	10 45

* Position of the compass changed since the earlier determinations.

Examples of permanency of ship's force on changes of geographic position are exhibited in the following vessels; in which, for the sake of comparison, the modulus has been multiplied by the horizontal intensity at the place.

Urgent.

Year.	Ship's force. Direction.	Amount.
1855. England	176	0·215
1855. Malta	184	0·189
1856. England	170	0·183

Megæra.

Year.	Direction.	Amount.
1852. England	150	0·238
1853. Antigua	145	0·213
1857. England	162	0·219

Triton.

Year.	Direction.	Amount.
1852. England	198	0·142
1852. Corfu	200	0·142
* 1857. England	213	0·178
* 1858. Fernando Po	181	0·188

Oberon.

Year.	Direction.	Amount.
1851. England	295	0·230
1856. Malta	297	0·201
* 1858. England	323	0·180
* 1858. Monte Video	303	0·179

Bloodhound.

Year.	Direction.	Amount.
1845. England	351	0·256
1846. Constantinople	347	0·281
1846. Athens	344	0·249

Assistance.

Year.	Direction.	Amount.
1857. England	129	0·259
1858. Canton	119	0·274

Adventure.

Year.	Direction.	Amount.
1857. England	124	0·305
1858. Whampoa, China	118	0·307

Caradoc.

Year.	Direction.	Amount.
1848. England	199	0·230
1852. Malta	189	0·258
1855. England	191	0·193
1857. Malta	191	0·229
1858. Malta	200	0·242

Industry.

Year.	Ship's force. Direction.	Amount.
1856. Malta	359°	0·240
1856. England	13	0·256

Sharpshooter.

Year.	Direction.	Amount.
1852. England	180	0·280
1853. Rio de Janeiro	189	0·253
1857. England	160	0·235
1857. Isles de Los, Africa	172	0·222

Jackal.

Year.	Direction.	Amount.
1845. England	353	0·288
1846. Athens	355	0·274
1847. Lisbon	352	0·260

Trident.

Year.	Direction.	Amount.
1846. England	363	0·345
1847. Malta	357	0·359
1848. England	360	0·359
1852. England	353	0·342
1852. Rio de Janeiro	351	0·368
1856. England	351	0·376
1857. Ascension Island	342	0·373
1857. Cape of Good Hope	354	0·333
1859. England	363	0·320

Harpy.

Year.	Direction.	Amount.
1854. England	5	0·152
1857. Malta	352	0·166

Wilberforce.

Year.	Direction.	Amount.
1843. England	223	0·185
1843. River Gambia	222	0·193

Torch.

Year.	Direction.	Amount.
1852. England	356	0·186
1852. Madeira	348	0·153
	352	0·161
1852 St. Vincent Island	350	0·198
1852. Rio de Janeiro	351	0·219
1852. Tristan d'Acunha	337	0·189
1852. Cape of Good Hope	3	0·190
1853. St. Paul's Island	357	0·198
1853. Swan River	358	0·182
1853. K. George's Sound	352	0·214
1856. Australia	3	0·246 approx.

* Position of compass changed since the earlier determinations.

The Torch is a special example. This vessel was sold out of Her Majesty's service at Sydney, after a continuous service of three years in Australia (1853 to 1856) in high south magnetic latitudes; in July 1856 she was chartered by the Colonial government of New South Wales to proceed to the northern coast of Australia to render assistance to an exploring expedition. The officer who had previously been in command, Lieut. Wm. Chimmo, R.N., was the Government agent on this occasion, and on the passage, especially along the eastern shores of Australia, that officer made numerous observations for the Variation of the Compass (the direction of the ship's head being noted to each), which were transmitted to the Admiralty. From these observations, compared with the well-known variation in these seas, I was enabled graphically to construct a curve of deviation: the results are given, and are confirmatory of the general permanent nature of the ship's magnetism under circumstances which I apprehend are novel, and not without value in a theoretical discussion.

The conclusions derived from a review of the foregoing results are not unimportant; and not the least of these in practical value, is that in an iron ship of ordinary dimensions, and of conditions similar to the examples quoted, a standard compass can be placed, the deviations of which will but little exceed those obtaining in wood-built steam-ships; and further, that on a change of geographic position, however great, these compass deviations will be within smaller limits, and can be approximately predicted.

A divergence from these conditions will arise when the inductive magnetism of the hull or machinery predominates. If we may judge from the case of the Royal Charter, whose magnetic elements have been so ably discussed by various authorities, large quadrantal deviation and fluctuating sub-permanent magnetism (due to hull alone) are coexistent, and give rise to conditions of compass-disturbance which are beyond prediction, have hitherto baffled inquiry, and given a complexion to theoretical deductions varying as regarded from different points of view.

Observations on the early changes of an Iron-built ship's Magnetism, illustrated by experiments in the Steam-Ship Great Eastern.

The opinion has been long entertained, that the original magnetism of an iron-built ship, or that acquired in the process of building, undergoes a rapid change after launching, and that from this cause accidents have occurred to recently launched and hastily equipped vessels. The records of ships of the Royal Navy do not illustrate this subject.

The unusual dimensions of the Great Eastern, and the interest attaching to the progress and success of so great an undertaking, pointed her out as a desirable ship to test in elucidation of various problems connected with the mariner's compass, and especially of the supposed early changes in the ship's magnetic force.

Through the kindness of the Directors, and partly in the nature of assistance sought for by that body from the Lords of the Admiralty, I was enabled to make many

observations, the results of which, so far as they relate to the early changes in the deviations of the compass, and the external magnetic lines of the ship, will be found in Table V., and an accompanying diagram in Plate XV.

In the progress of building (18th August, 1857), I ascertained by astronomical bearings, with the known variation of the compass at the time, that the magnetic direction of her keel and head was S. 29° 50′ E. A short time previous to the launching (November 1857), I also obtained the few results for the external magnetic lines, which will be found in the diagram.

After launching, the Great Eastern was secured near Deptford dockyard, with her head S. 46° E. magnetic; differing only 16° from the original direction while building; considerable works, chiefly internally, were in progress till the time of quitting this anchorage. In August 1859, a few days prior to leaving the river, an extended series of observations for the development of the external magnetic lines (see diagram, Plate XV.) was obtained; which show that some alteration had taken place since the first approximate determination.

On September 7th, 1859, the Great Eastern quitted Deptford on her preliminary trip to Portland, arriving at the latter port on the 10th. On the passage between these places, which included temporary anchorages at Purfleet and the Nore, every opportunity was embraced of determining the deviations of the compass at various selected stations in the ship which are marked in the diagram. The deviations whilst in the River Thames were determined by noting the difference between the bearing of the ship's head, as astronomically determined (by the use of a repeating card, and prepared table of the sun's bearings), and as denoted by the compass: a curve of deviations embracing each point of the compass was then graphically drawn through the general results.

At Portland, lying within the breakwater, the correct magnetic bearing of St. Alban's Head, a distant point of land, afforded ready means of determining the deviations as the vessel swung round at her anchor; and subsequently at Holyhead, where I proceeded again in conjuction with Mr. RUNDELL, similar means were adopted as at Portland by the bearing of a distant Welch mountain. As it was not possible to "swing" the Great Eastern, from her ponderous bulk, in the mode usually adopted under these circumstances with ordinary sized vessels, we were dependent on the changes of ship's head arising from winds and tides: this necessarily occupied much time, and was the occasion of gaps being left in the curves of deviations obtained both at Portland and Holyhead, which required to be arbitrarily filled up. As these curves presented no anomalous differences from those of ordinary sized ships, but were marked by perfect regularity and consistency among the observations, these gaps were confidently completed.

From a consideration of the magnetic character of the Great Eastern, it is apparent that the Admiralty Standard compass, as also the ship's Standard compass, were placed in the best position with respect to the hull and machinery, both for experimental research and the navigation of the ship; indeed, from the vast amount of machinery and neces-

sarily inductive material running nearly fore and aft the vessel, I am disposed to attach but little comparative value to any of the results except those of the Admiralty Standard compass, as it will be seen that the other compasses are influenced by the near proximity of steam funnels or iron masts.

Directing attention to the changes in the magnetism of the ship as indicated by this compass, the gradual diminution of the ship's force is marked at each successive period of observation, and also the constant tendency to attain a fore-and-aft direction. In the first five days, from Deptford to Portland, the force had diminished from 0·585 to 0·480, nearly one-fifth, or the semicircular deviation decreased from 35° 50′ to 28° 45′; the direction of force, or neutral points, approaching a fore-and-aft line 10°, or from 47° on the starboard bow to 37°: it is here worthy of remark, that the general direction of the ship's head for three days at Portland out of the five named, was N.W., or exactly opposite to her direction whilst lying at Deptford.

The change at the expiration of the next six weeks, the ship in the interim having made the passage to Holyhead, with some trifling rough weather, still shows a diminution of force, and tendency to the fore-and-aft direction of the neutral points of disturbance: the former is reduced from 0·480 to 0·390, or about one-sixth (the corresponding semicircular deviation being 28° 45′ and 23° 0′); and the latter changed 5°, or from 37° to 32°.

The changes denoted by the mast and platform compasses do not follow the same progressive decrease and change of direction of ship's force. To the less perfect observations of the mast-compass, arising from the difficulty of obtaining readings aloft, and from the friction of blunted pivots after a few weeks' wear and tear, can be traced the probable causes for this instrument; the unfavourable but unavoidable position for the platform compass has been adverted to.

The quadrantal deviations of all the compasses show a decrease, so far confirmatory of the law that exists in the numerous vessels reviewed; but there is an anomaly detected by Mr. Airy* in the quadrantal disturbance of the Admiralty Standard compass worthy of record, viz. that it is larger in the quadrant from west to north; the position opposite to that in which the ship was built.

	1st, or N.E. quadrant.	2nd, S.E.	3rd, S.W.	4th, N.W.
River Thames . .	+4° 33′	−2° 40′	+4° 8′	−6° 6′
Portland	+4 38	−3 8	+4 53	−6 37

Indication of rapid changes in the ship's magnetism was also given by the ship's established standard compass, which had been compensated on the passage down the river Thames (from the known direction of the ship's head by astronomical bearings), and deemed by the gentlemen engaged for the purpose as correct. At Portland, with head in the N.W. direction, it had 7° error on the second day at that anchorage.

* Communicated in a letter to Mr. Rundell, Secretary of the Liverpool Compass Committee.

This error, as also a smaller one considered to exist after the ship's arrival at Holyhead, was, as I understood, eliminated prior to my visit at that port in the latter part of October; but on then determining the deviations of the Admiralty Standard compass, and referring the results to the ship's compensated standard, a residual error in the latter of nearly 5° still existed on some of its points.

[Although the question of compensation is extraneous to the general tenor of this Report, I deem it of interest to record the above circumstances, to correct a misapprehension as to the employment of long needles, carried, in the compasses of the Great Eastern, to the extent of 11 inches for standard and steering, and 16 inches for the mast-compass. A series of experiments, still in progress, which I have instituted in elucidation of the comparative errors due to the use of long and short needles, both where the disturbing cause is comparatively close to the compass, as in the case of the rudder-head near the steering compass, or the top sides and iron* beams when heeling, and in compensated compasses from the necessary proximity of bar magnets, lead to the conclusion that no compass-needle should exceed in length, for service in an iron ship, 6 or 7 inches; the card of course may be enlarged as practically convenient.

The errors of long needles, under the conditions just named, of proximity to permanent magnetic bodies, arise from this notable fact, that their deviations assume the form, not of a curve which is simply "semicircular," as the curve is found to be which results from the ship's general magnetic force when the length of the needle may be relatively considered as infinitesimally small, but of a "sextantal" superposed on a "semicircular" curve, the various maxima of the "sextantal" curve increasing with the square of the length of the needle. Assuming the zero of both curves (the semicircular and sextantal) to be at the magnetic North and South, the maxima of the sextantal deviations (by ship's compass) are respectively at about N. 30° E., East, S. 30° E., S. 30° W., West, N 30° W., the points of coincidence with the semicircular curve being at North, N. 60° E., S. 60° E., South, S. 60° W., and N. 60° W.]

The tendency of the direction of the ship's force in the Great Eastern is to assume a fore-and-aft line, supporting the view, that time, with the vibrations and concussions due to sea-service, leads to a settled distribution of the magnetic lines; the respective sections of the hull which have north and south polarity being separated by lines approximating more nearly to a horizontal equatorial plane through the body of the ship, instead of the inclined equatorial plane of separation due to the magnetic dip of the locality, and divergence from the magnetic meridian of the hull while building.

A similar tendency of the direction of the ship's force to approach a fore-and-aft line will be observed in several examples of Table I.

The example of the Great Eastern offers this practical information; that prior to a newly built iron ship being sent to sea, her head (while being equipped) should be secured in an opposite direction to that in which she was built; and that the magnetic lines should be assisted to be "shaken down" by the vibrations of the machinery in a short preparatory trip prior to the determination of her compass errors, or their com-

pensation; but especially that on the early voyages vigilant supervision should be exercised in the determination of the compass disturbances.

Another important point, which is generally neglected when compasses are adjusted by the aid of magnets in a newly built iron ship, is rendered manifest from the circumstances just detailed, namely, the necessity of the errors of the compass arising from the iron in a ship being determined and placed on record prior to its adjustment. Without the knowledge, to be derived from these observations, of the magnetic force of the ship, or the local disturbing cause (if such exists), all future changes of magnetism, and consequent errors of the compass, are the merest guesswork, both to those who adjust and the authorities in charge of the navigation of the ship.

Any future legislation for the security of the navigation of our mercantile marine with reference to iron-built ships, should secure the determination and record of these preliminary observations.

I have alluded to the importance of the conclusions to be derived from a review of the examples and cases given in this Report; for although varying conditions of compass disturbance exist, and the inference is irresistible that they arise from the nature of the iron employed in the construction of the hull of the ship, there is no doubt that, by attention to a few leading principles in the building and equipment of iron ships, the larger and uncertain sources of error may be modified and reduced within limits both of fluctuation and amount, that will not seriously compromise the safety of the ship in the hands of an ordinarily prudent seaman.

The points of practical import to which I would invite attention are,—

1st. The best direction, with reference to the magnetic meridian, for the keel and head of an iron ship to be placed for building, to ensure the least compass disturbance.

2nd. The best position and arrangement for a compass, to ensure small deviations, and permanency on changes of geographic position.

3rd. The changes to which the compass is liable from various causes when the foregoing conditions are fulfilled.

Before entering on these points, I would refer to an appended series of diagrams (Plate XVI.) illustrative of the polarity of the topsides (and the coefficients B and C), according to the direction of the build; these diagrams forming the key to much that comes under review.

1. *On the best Direction for Building an Iron Ship.*

In those built head N.E., East, West, and N.W., strong *south* polarity (or an *attractive* force on the north end of the compass needle) obtains on one side of the ship adjoining the compass as usually placed between the middle section and the stern; the resulting disturbance is not lessened as the compass is moved in a fore-and-aft line within these limits.

In vessels built head S.E. and S.W., *north* polarity obtains under the same conditions.

In vessels built head North or South, the conditions arise, that in the former the attraction is toward the stern (the topsides in their action being neutral to a compass in the middle line of the deck), and diminishes in force as the compass is moved towards the bow. In the latter the law is reversed, and small compass deviations are obtained as the stern is approached.

In an iron *sailing* ship, built head to South, there will be an attraction of the north point of the compass to the head, and if built head to North, a like attraction to the ship's stern; and so far there would seem to be no advantage in one direction over the other. But in the first case the topsides near the compass have weak magnetism; in the second case they are strongly magnetic: the first position seems therefore preferable.

In an iron steam-ship, built head to the South, the attraction due to machinery is added to that of the hull, whereas in one built head to the North, the attractive forces of hull and machinery are, in the northern hemisphere, antagonistic, and a position of small, or no "semicircular" deviation for the compass may generally be obtained. To iron steam-vessels engaged on the home or foreign trades in the northern hemisphere, this direction of build is therefore to be preferred.

2. *On the Position and Arrangements for the Compass.*

The position of compasses, whether standard or steering, must depend, as will have been observed from the foregoing conclusions, on the direction of the ship's build; that is, in those built head North the compass must be as far removed from the stern as circumstances will permit; in those built South, placed as near to the stern as convenient, without approaching so close to the rudder-head or iron taffrail as to cause the ship's general magnetism to be overpowered by the magnetic influence of those masses.

In ships built East or West there is little choice of position, except to avoid, as a general rule, proximity to vertical masses of iron; in vessels built with their heads on the intercardinal points, a position approximating to the bow or stern respectively, where the action from the topsides (to be determined experimentally) is at a minimum, is to be preferred.

Ample elevation above the deck, and to be strictly confined to the middle line of the ship, are the primary conditions of position for every compass in an iron ship, and no compass, whether steering or standard, should be nearer the iron deck beams than 4 feet*: for the steering compass this arrangement could be met by the use of a vertical card for the helmsman.

The standard compass, which as a rule I should recommend to be invariably uncompensated, requires an elevation of at least 5 or 6 feet from the deck, and to be fitted on

* A curious illustration of the effect of iron deck beams on long and short compass-needles resulted from some experiments made on board H.M.S. Bloodhound: on the deck, or within a few inches of the position where, not unfrequently, hanging or tell-tale compasses are placed, a 10-inch needle had 43°, a 6-inch needle 38°, and a 1½-inch needle 33° difference from their uniform deviation at 1 foot 9 inches from the deck.

a separate and permanent pillar or stand: it is by this superior elevation that the strong magnetic power of the iron beams and adjoining topsides are correspondingly lessened.

As every piece of iron not composing a part of, and hammered in the fabrication of the hull,—such as the rudder, funnel, boilers and machinery, tanks, cooking galleys, fastenings of deck houses, &c.,—are all of a magnetic character differing from the hull of a ship, their proximity should be avoided, and, so far as possible, the compass should be placed so that they may act as correctors of the general magnetism of the hull.

A compass placed out of the middle line of the deck is affected by the nearest topside, and its deviations must necessarily be much increased if that topside has the dominant polarity, as in ships built East or West.

Experience has proved that the practical value of mast or elevated compasses has in some cases been overrated; they are, in fact, affected by the ship's magnetism to an amount depending on their elevation and the direction of the ship's build: thus in ships built North or South, but especially the latter—the compass being on the mizen mast—the deviations will be large comparatively. In ships built East or West the deviations will be comparatively small, from the topside, which would affect a deck compass, being more directly under the mast-compass; they may therefore be useful in the latter cases, and valueless in a ship built head to the South. The wear and tear on the pivots and agate caps of mast-compasses, from the increased motion due to their elevation, require constant attention when they are employed.

3. *On various Sources of Error affecting a Compass placed under favourable conditions.*

Errors arising from changes of geographic position, as also incidental causes of error due to anomalous rather than general conditions, have been brought under review in the general progress of this Report. There is, however, one source of compass-error—that arising from the heeling of the ship—which has not been alluded to, as the ship in all the points hitherto reviewed is assumed to be on an even keel.

The few experiments made in ships of the Royal Navy will be found in Table I., and they tend to prove, as also does the test of experience, that when the original compass deviations are small, the errors from heeling are generally small in proportion; and conversely, that exaggerated errors from heeling are the consequence of exaggerated errors while on an even keel. Ample elevation from the deck, in order to raise the compass above the level of the topsides and adjacent deck beams, is one of the chief conditions for reducing this source of error.

The action of the topside nearest to the compass when the ship is heeled is well marked in the examples of the ships Bloodhound and Sharpshooter, the former with +B, or head built to South, and the latter with −B, or head built to North; in the Bloodhound the north end of the needle is drawn to *leeward*, in the Sharpshooter to *windward*. In the iron sailing-brig Recruit, with +B, the effect is the same as in the Bloodhound.

From the diagrams illustrative of the polarity of an iron ship's topsides, the action of

the latter on the compass in heeling may be gathered, and the corresponding effect shown, under the various directions of the ship's head in building: thus—

With head built	North,	on heeling,	the north end of compass needle will be *attracted* to the weather or nearest side from its *south* polarity.
,,	N.E.,	,,	,, the same.
,,	East,	,,	,, the same.
,,	S.E.,	,,	the north end of needle will have but little error from the balanced conditions of north and south polarity of topsides.
,,	South,	,,	the north end of needle will be *repelled* to the lee side by the *north* polarity of nearest or weather topside.
,,	S.W.,	,,	the north end of needle will have but little error, as at S.E.
,,	West,	,,	the north end of needle will be *attracted* to the weather or nearest side.
,,	N.W.,	,,	,, the same*.

These laws only hold good as long as the topsides in the immediate vicinity of the compass retain their dominant polarity due to their original direction of build in Great Britain: if in south magnetic latitudes a change of polarity takes place, the conditions of heeling correspond to such change.

The maximum disturbance on heeling in all these vessels is when their heads are (by disturbed compass) magnetic North or South, and this disturbance vanishes when the head is East or West. This law of disturbance may be thus explained: when the vessel's head is north or south on an even keel (by disturbed compass), the needle lies parallel to the topsides by their combined action, which neutralizes each other; on heeling, the nearest topside exercises its then dominant polarity at right angles to the direction of the needle, and hence the maximum error. With the ship's head east or west, whether on an even keel or heeling, either pole of the compass-needle points directly to the topsides, and is consequently unaffected except in a vertical plane.

As the amount of disturbance on heeling varies under the various conditions of direction of build, height of compass, and breadth of ship or distance of topsides, added to the prevailing permanent or inductive magnetic condition of the latter and the deck beams, each ship must have an individual character, to be determined only by experiment or observation at sea. There are, however, strong grounds for inferring that by a

* These principles have in their main features been confirmed by the experiments and investigations of the Secretary of the Liverpool Compass Committee,—Mr. RUNDELL,—to whom I am indebted for much valuable information on many questions of theoretical and practical value; but their simple illustration by a consideration of the appended diagrams, which, so far as I am aware, are novel in their application, will probably be found instructive and useful to the practical seaman.

judicious position of the compass, so as to ensure small errors while on an even keel, the errors arising from the ship's heel will be so proportionally reduced, as not practically to affect the navigation of the ship in the hands of a prudent seaman.

In concluding this Report, which in some of its details will, I trust, be found to narrow the grounds of inquiry in this interesting branch of science, so important in its practical relations to a maritime nation rapidly expanding its iron commercial navy, I beg leave to record the material assistance I have derived from the researches of the Astronomer Royal and ARCHIBALD SMITH, Esq., on the subject of a ship's magnetism. Without their skilful analysis and mathematical demonstrations, and much personal assistance rendered by the latter gentleman, I could not have approached the subject, and can therefore claim but little merit,—except that due to the labours of a lengthened computation, and some practical experience and close observation,—in the elucidation of whatever principles may be received as sound in practice and as additions to science.

I have the honour to be,

Sir,

Your obedient Servant,

FREDK. J. EVANS, Master R.N.

To Captain WASHINGTON, *R.N., F.R.S.,*
Hydrographer to the Admiralty.

Appendix.

No. I.

The Admiralty Standard Compass.

The chief points in the construction of this instrument are the following:—

1. The *bowl* is constructed of stout copper with the view to calm the vibrations of the needle, and the intersecting point of the axis of its gimbals is made to coincide with the point of suspension of the card, and also with the centre of the azimuth circle.

2. The *azimuth circle* is accurately graduated to minutes of arc, and may be used in addition on shore for surveying purposes: thus when accurate magnetic bearings are required, the zero of the circle may be adjusted to the magnetic north, shown by the card, and then clamped; any number of magnetic bearings may then be obtained round the circle: or by adjusting the zero of the circle to any given object and clamping the compass to its stand, the angles of objects round the horizon may be observed and read off to the nearest minute.

In observing Amplitudes and Azimuths, the bearings are read from the card without reference to the azimuth circle, the card being graduated to 20 minutes.

3. The *magnetic needles* employed are compound bars, formed of laminæ of that kind of steel (clock-spring) which has been ascertained by numerous experiments to be capable of receiving the greatest magnetic power. Each compass has two cards, A and J; the former is used at all times, except in stormy weather with much motion in the ship, when the heavy or J card is substituted.

Each *card* is fitted with four needles fixed vertically and equidistant on a light framework of brass screwed to the card; the pair of central needles are 7·3 inches long, and the pair of external ones 5·3 inches, the whole weight of the A card being 1525 grains*. The pivots for the needles are pointed with "native alloy," as being harder than steel, and not subject to corrosion by exposure to the atmosphere; the ruby cap of the card is worked to a form to suit these points.

4. The *impressions of the cards* are taken after the paper has been cemented to the mica plate forming the basis; distortions from shrinking are thus prevented and a more perfect centering attained.

Finally. The cards and needles are adjusted to the magnetic meridian at the Compass Observatory for Her Majesty's Navy at Woolwich, a place free from the local influence of iron. The various adjustments for centering, and the elimination of errors

* In order that a vibration communicated to a card about a diameter intermediate between the N. and S., and the E. and W. diameters, may not give rise to a "wabbling" motion, the moment of inertia of the card about these two diameters should be the same. It was shown by Mr. Archibald Smith that this is the case with any two parallel needles of uniform thickness forming chords of the same circle, if their extremities are separated by 60°; consequently, with any four such needles, if their extremities are separated by 30°; and the needles of the Admiralty Standard compasses have been uniformly so arranged.

due to displacement of sight-vanes, and prism, are also made at this observatory, the compass being afterwards supplied to Her Majesty's ships perfectly free from error.

No. II.

Table of Magnetic Elements (Terrestrial).

Place.	Inclination, or Dip.		Total Intensity, in 1840.	Horizontal intensity.					
			Arbitrary scale.	Arbitrary scale.	Scale adopted in Report.	On the authority of Mr. Airy.	Scale adopted in Report.	By Gauss.	Scale adopted in Report.
			b	*c*		*d*		*e*	
From Magnetic Survey of the British Islands:—	Year.		Year.						
Greenwich	1837	+69° 17′	1859 +68° 25′	1·372					
Greenhithe	,,	+69 15		1·370		3·79			
Sheerness	,,	+69 12		1·369		3·78			
Portsmouth	,,	+69 2		1·370	= 0·508 or 1·000	3·83	3·80 or 1·000	515 or 1·000	
Portland	,,	+69 7		1·372					
Plymouth	,,	+69 16		1·375		3·82			
Holyhead	,,	+70 52		1·395					
River Tagus	1840*a*	+64 0	1858 +60 39*f*	1·35	= 0·634 or 1·248	4·62	or 1·217	615 or 1·194	
Malta	,,	+52 0		1·21	,, 0·745 ,, 1·467	5·74	,, 1·510	750 ,, 1·456	
Corfu	,,	+55 0	1857 +55 42*g*	1·21	,, 0·694 ,, 1·366			750 ,, 1·456	
Athens	,,	+51 0		1·20	,, 0·755 ,, 1·486	5·85	,, 1·539	740 ,, 1·437	
Constantinople	,,	+54 0		1·22	,, 0·717 ,, 1·411	5·63	,, 1·482	760 ,, 1·495	
River Danube, St. George's Mouth	,,	+60 0		1·25	,, 0·625 ,, 1·230			715 ,, 1·388	
Madeira	,,	+60 30	1847 +59 42	1·34	,, 0·680 ,, 1·339			660 ,, 1·281	
St. Vincent, Cape de Verd Islands	,,	+45 0		1·18	,, 0·805 ,, 1·585			805 ,, 1·563	
River Gambia	,,	+38 30		1·15	,, 0·900 ,, 1·771			830 ,, 1·592	
Isles de Los	,,	+33 30		1·11	,, 0·925 ,, 1·821			830 ,, 1·611	
Fernando Po	,,	0 0		0·95	,, 0·977 ,, 1·923			875 ,, 1·700	
Ascension Island	,,	+ 0 30		0·90	,, 0·850 ,, 1·673			830 ,, 1·611	
Tristan d'Acunha	,,	−43 0		0·90	,, 0·658 ,, 1·295			700 ,, 1·361	
Cape of Good Hope	,,	−53 20	1857 −54 42*h*	0·98	,, 0·576 ,, 1·148	4·46	,, 1·174	630 ,, 1·204	
St. Paul's (Indian Ocean)	,,	−68 0		1·50	,, 0·562 ,, 1·106			610 ,, 1·185	
Kurrachee	,,	+28 15		1·16	,, 1·022 ,, 2·012			1010 ,, 1·961	
Hong Kong	,,	+30 20	1858 +31 26*h*	1·22	,, 1·041 ,, 2·049			1000 ,, 1·942	
Canton	,,	+31 30	1858 +32 35*h*	1·25	,, 1·040 ,, 2·049			1000 ,, 1·942	
Shanghai	,,	+44 0	1857 +45 18*h*	1·31	,, 0·921 ,, 1·813			925 ,, 1·796	
Apia, Upolu I. (Pacific Ocean)	,,	−35 30		1·30	,, 1·058 ,, 2·083			980 ,, 1·903	
Sydney, New South Wales	,,	−62 45	1849 −62 45	1·67	,, 0·765 ,, 1·506			870 ,, 1·689	
Port Nicholson, New Zealand	,,	−65 0	1850 −64 52	1·66	,, 0·702 ,, 1·382			855 ,, 1·660	
King George's Sound	,,	−65 0	1845 −65 12	1·69	,, 0·714 ,, 1·406			765 ,, 1·485	
Swan River, Australia	,,	−62 30	1846 −63 6	1·64	,, 0·757 ,, 1·490			785 ,, 1·524	
Sydney, Cape Breton Island	,,	+76 30		1·68	,, 0·392 ,, 0·772			370 ,, 0·719	
St. John's, Newfoundland	,,	+76 0		1·63	,, 0·394 ,, 0·776			355 ,, 0·689	
Halifax, Nova Scotia	,,	+75 45	1847 +75 37	1·70	,, 0·418 ,, 0·823			400 ,, 0·777	
Penetanguishine, Lake Huron	,,	+76 0	1844 +76 30	1·84	,, 0·445 ,, 0·876			395 ,, 0·767	
Antigua	,,	+50 0		1·38	,, 0·887 ,, 1·746			840 ,, 1·631	
Rio de Janeiro	,,	−12 30	1857 −11 21*h*	0·86	,, 0·841 ,, 1·675	6·49	,, 1·708	860 ,, 1·670	
Monte Video	,,	−35 0	1853 −32 7*i*	1·06	,, 0·898 ,, 1·768	6·16*i*	,, 1·602	835 ,, 1·621	
Callao	,,	− 7 0		1·00	,, 0·997 ,, 1·963			1000 ,, 1·942	
Valparaiso	,,	−38 30	1857 −35 37*k*	1·17	,, 0·934 ,, 1·838	7·17	,, 1·887	865 ,, 1·680	
Sandwich Islands, Honolulu	,,	+40 30	1857 +42 0*k*	1·10	,, 0·817 ,, 1·628			890 ,, 1·728	
Vancouver Island, Esquimalt	,,	+72 0	1858 +71 55*k*	1·70	,, 0·528 ,, 1·040			500 ,, 0·971	
,, Nanaimo	,,	+72 20		1·70	,, 0·516 ,, 1·016			495 ,, 0·961	

a, *b* On the authority of General Sabine, from Keith Johnston's Physical Atlas, Second Edition, "Terrestrial Magnetism."

c Computed from the formula $X = R \cos \theta$, in which R denotes the total intensity, X its horizontal component, and θ the dip.

d Philosophical Transactions for 1856, Mr. Airy "On the Observed Deviations of the Compass in Wood-built and Iron-built Ships.'

e From the Atlas des Erdmagnetismus of Gauss. Leipzig, 1840.

f Dr. J. Lamont, "Erdmagnetismus an verschiedenen Puncten des Südwestlichen Europa." Munich, 1858.

g Dr. F. Schaub, "Magnetische Beobachtungen im Östlichen Theile des Mittelmeeres." Trieste, 1858.

h From Captain Shadwell, R.N., Her Majesty's Ship Highflyer.

i From Lieutenant Gilliss, United States Navy.

k From Captain G. H. Richards, R.N., Her Majesty's Surveying Ship Plumper.

Table I.—Iron-built Ships, Her Majesty's Navy.

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients. A.	D.	E.	Coefficient B.	Ship's force to Head. Earth's horizontal force =1·000.	Coefficient C.	Ship's force to Starboard. Earth's horizontal force =1·000.
Feb. 25, 1855.	Portsmouth	Himalaya, 3453	+0° 46′	+3° 51′	+0° 21′	−15° 58′	−0·2751	− 0° 33′	−0·0096
Nov. 21, 1856.	Plymouth		+0 30	+2 48	+0 32	−14 3	−0·2428	− 0 23	−0·0067
July 4, 1859.	Plymouth		+0 20	+3 18	−0 10	−14 5	−0·2433	+ 2 53	0·0503
Sept. 21, 1855.	Sheerness	Urgent, 1981	+0 4	+2 58	+0 10	−12 20	−0·2136	+ 0 58	0·0169
Nov. 7, 1855.	*Malta*		+0 54	+3 6	−0 34	− 7 10	−0·1247	− 0 31	−0·0090
June 25, 1856.	Plymouth		−0 20	+2 45	−0 5	−10 23	−0·1802	+ 1 51	0·0323
Oct. 29, 1857.	Portsmouth		+0 32	+2 22	−0 11	− 8 43	−0·1515	+ 3 34	0·0622
Oct. 11, 1859.	Portsmouth		+0 38	+2 12	−0 9	− 8 32	−0·1484	+ 1 37	0·0282
Feb. 19, 1852.	Portsmouth	Simoom*, 1980	+0 11	+3 57	−0 9	+20 5	0·3434	− 7 15	−0·1262
Sept. 28, 1852.	Portsmouth		−0 9	+4 33	−0 19	+20 7	0·3439	− 7 18	−0·1271
Feb. 1853.	*Cape of Good Hope*		−1 47	+4 13	+0 22	+13 6	0·2266	− 2 23	−0·0416
Jan. 13, 1857.	Portsmouth		−0 6	+3 50	−0 10	+18 51	0·3231	− 1 35	−0·0276
Nov. 5, 1859.	Portsmouth		+0 23	+3 25	−0 50	+18 23	0·3154	+ 1 14	0·0215
June 14, 1855.	Portsmouth	Perseverance, 1967	+0 4	+3 18	+0 30	− 6 39	−0·1158	+ 1 33	0·0270
Mar. 13, 1856.	Portsmouth		+0 52	+2 53	+0 20	− 7 32	−0·1311	+ 1 45	0·0305
Aug. 10, 1858.	Portsmouth		+0 10	+1 51	+0 5	− 5 19	−0·0926	+ 0 10	0·0029
Oct. 8, 1859.	Portsmouth		+0 30	+2 0	−0 10	− 5 5	−0·0886	+ 2 25	0·0422
Aug. 31, 1855.	Greenhithe	Transit, 2587	−0 12	+3 12	−0 8	+13 40	0·2363	+ 0 13	0·0038
Mar. 17, 1857.	Portsmouth		−0 44	+3 12	−0 2	+10 47	0·1871	+ 2 49	0·0491
May 4, 1857.	Portsmouth	Assistance, 1820	−0 8	+3 35	+0 1	−13 0	−0·2249	+11 49	0·2048
May 11, 1857.	Portsmouth	†	+0 12	+3 36	+0 19	− 9 28	−0·1645	+11 29	0·1991
Feb. 24, 1858.	*Canton River, China*		+0 23	+3 24	+0 30	− 3 47	−0·0660	+ 6 42	0·1167
May 9, 1857.	Portsmouth	Adventure, 1794	−0 45	+3 40	−0 7	− 9 52	−0·1714	+14 38	0·2526
1858.	*Whampoa, China*		−0 20	+3 0	−0 27	− 4 0	−0·0697	+ 7 38	0·1328
Feb. 21, 1851.	Sheerness	Vulcan, 1764 F.U.‡	+0 38	+3 20	+0 20	− 9 15	−0·1607	+ 1 55	0·0334
Sept. 30, 1851.	Portsmouth	F.D.	+0 29	+3 0	+0 11	− 8 37	−0·1498	+ 2 12	0·0384
			+0 15	+3 0	+0 18	− 9 25	−0·1636	+ 2 18	0·0401
July 1, 1852.	Portsmouth		−0 13	+3 37	−0 44	− 8 47	−0·1527	+ 0 43	0·0125
Nov. 19, 1852.	*Sydney, New South Wales*	F.D.	−0 16	+2 3	+0 55	−13 39	−0·2360	+ 2 43	0·0474
Feb. 1853.	*Cape of Good Hope*		+1 8	+4 15	+0 51	−16 3	−0·2765	+ 1 19	0·0230
May 26, 1853.	Portsmouth	F.U.	+0 31	+3 5	+0 16	− 8 28	−0·1472	+ 3 11	0·0555
June 19, 1854.	Portsmouth	F.U.	+0 16	+3 29	−0 53	− 1 40	−0·0291	+ 3 6	0·0541

* Head built S. 30° W. magnetic. Keel at an angle of 2° 15′ from horizontal plane.

† Standard compass changed in its elevation from deck 1 foot 11 inches; diminishing ship's force one-seventh.

‡ F.U. Funnel up. F.D. Funnel down.

Table I.—Iron-built Ships, Her Majesty's Navy.

Resultant of B and C, or ship's Total force.		Magnetic elements.		Position of standard compass.			Beams.	Horse-power and engines.	Where built.	Date of launching.
Direction.	Amount.	Horizontal force.	Dip, and nat. tang.	From funnel.	From taffrail.	Height from deck.				
				ft. in.	ft. in.	ft. in.				
182	0·275	1·000	+68° 25′ 2·53	113 0	62 0	8 4	Iron.	700, Screw.	Blackwall.	1854.
181½	0·243	1·000	+68 25 2·53	113 0	62 0	8 4				
168½	0·248	1·000	+68 25 2·53	113 0	62 0	8 4				
175½	0·215	1·000	+68 25 2·53	91 0	72 0	5 0	Poop-deck, wood.	450, Screw.	Blackwall (Mare and Co.).	3rd April, 1855.
184	0·125 0·189	1·510	+52 0 1·28	91 0	72 0	5 0				
170	0·183	1·000	+68 25 2·53	91 0	72 0	5 0				
157½	0·163	1·000	+68 25 2·53	91 0	72 0	5 0				
169½	0·151	1·000	+68 25 2·53	91 0	72 0	5 0				
340	0·367	1·000	+68 25 2·53	55 4	33 10	4 2½	Poop-deck, wood.	350, Screw.	Glasgow (R. Napier).	24th May, 1849.
340	0·367	1·000	+68 25 2·53	55 4	33 10	4 2½				
350	0·231 0·270	1·174	−54 42 − 1·41	55 4	33 10	4 2½				
355	0·326	1·000	+68 25 2·53	55 4	33 10	4 2½				
4	0·316	1·000	+68 25 2·53	56 4	31 6	4 6				
167	0·119	1·000	+68 25 2·53	97 0	71 0	4 3	Poop-deck, wood.	360, Screw.	Blackwall (Mare and Co.).	13th July, 1854.
167	0·134	1·000	+68 25 2·53	97 0	71 0	4 3				
178	0·093	1·000	+68 25 2·53	88 0	67 0	5 4				
154½	0·098	1·000	+68 25 2·53	88 0	67 0	5 4				
1	0·236	1·000	+68 25 2·53	105 0	72 0	4 6	Poop-deck, wood.	500, Screw.	Blackwall (Mare and Co.).	20th Mar. 1855.
15	0·194	1·000	+68 25 2·53	105 0	72 0	4 6				
138	0·304	1·000	+68 25 2·53	122 0	30 0	4 5	Iron.	400, Screw.	Birkenhead (Laird).	5th April, 1855.
130	0·259	1·000	+68 25 2·53	122 0	30 0	6 4				
120	0·134 0·274	2·049	+32 35 0·63	122 0	30 0	6 4				
124	0·305	1·000	+68 25 2·53	125 0	30 0	6 4	Iron.	400, Screw.	Birkenhead (Laird).	17th Feb. 1855.
118	0·150 0·307	2·049	+31 30 0·61	125 0	30 0	6 4				
168½	0·163	1·000	+68 30 2·54	27 10	49 8	5 0	Poop-deck, wood.	350, Screw.	Blackwall (Ditchburn and Mare).	27th Jan. 1849.
166	0·154	1·000								
166½	0·168	1·000	+68 30 2·54	27 10	49 8	5 0				
175½	0·153	1·000	+68 30 2·54	27 10	49 8	5 0				
168½	0·241 0·363	1·506	−62 45 − 1·94	27 10	49 8	5 0				
175	0·278 0·326	1·174	−54 42 − 1·41	27 10	49 8	5 0				
160	0·157	1·000	+68 30 2·54	27 10	49 8	5 0				
118	0·062	1·000	+68 30 2·54	27 10	49 8	5 0				

TABLE I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Date.	Place of observation.	Ship's name and tonnage.	Permanent coefficients.			Coefficient	Ship's force to Head. Earth's horizontal force =1·000.	Coefficient	Ship's force to Starboard. Earth's horizontal force =1·000.
			A.	D.	E.	B.		C.	
Apr. 17, 1856.	Portsmouth	VULCAN, 1764 ..... *continued.*	−0° 9′	+3° 1′	−0° 3′	− 2° 37′	−0·1395	+ 3° 35′	0·0619
Nov. 6, 1856.	Sheerness	F.U.	+0 27	+1 55	+0 21	− 5 4	−0·0883	+ 3 50	0·0668
Sept. 4, 1857.	Portsmouth	F.U.	+0 30	+2 56	−0 3	− 1 58	−0·0343	+ 4 58	0·0866
		F.D.	+0 13	+2 55	−0 16	+ 0 51	0·0148	+ 5 11	0·0903
Aug. 16, 1859.	Portsmouth	F.U.	+0 40	+2 48	+0 28	− 4 20	−0·0756	+ 9 37	0·1670
		F.D.	+0 36	+2 51	+0 5	− 1 34	−0·0273	+ 9 25	0·1636
Oct. 22, 1851.	Sheerness	MEGÆRA, 1395 F.D.	−0 15	+1 46	+0 32	−12 43	−0·2201	− 2 5	−0·0363
		F.U.	+0 3	+2 32	−0 8	−13 5	−0·2264	− 3 12	−0·0558
Sept. 11, 1852.	Sheerness		−0 24	+1 15	+0 29	−11 52	−0·2056	+ 6 52	0·1196
Dec. 8, 1853.	*Antigua*		+0 5	+1 36	−0 5	− 5 46	−0·1005	+ 3 58	0·0692
Jan. 23, 1857.	Portsmouth		+0 46	+1 48	−0 23	−12 1	−0·2082	+ 3 51	0·0671
Jan. 20, 1847.	Greenhithe	BIRKENHEAD, 1405	+0 18	+2 53	−0 11	−13 51	−0·2394	− 6 27	−0·1123
Feb. 19, 1847.	Portsmouth		−0 14	+2 44	+0 25	−13 51	−0·2394	− 6 39	−0·1158
Mar. 20, 1848.	Portsmouth		−0 29	+2 48	+0 23	−13 30	−0·2334	− 6 32	−0·1138
1850.	Portsmouth		−0 30	+2 13	+0 22	−13 36	−0·2351	− 6 54	−0·1201
Feb. 17, 1851.	Portsmouth		−0 33	+2 12	+0 27	−13 51	−0·2394	− 6 48	−0·1184
Aug. 10, 1846	Greenhithe	TRIDENT, 850	+0 38	+4 3	+0 45	+20 8	0·3442	+ 1 13	0·0212
1847.	*Malta*		+0 25	+3 46	+0 30	+13 38	0·2357	− 2 0	−0·0349
May 23, 1848.	Greenhithe		+0 37	+3 52	+0 21	+21 1	0·3586	− 0 13	−0·0038
Oct. 17, 1849.	Plymouth		+0 25	+3 31	−0 6	+18 26	0·3162	− 0 2	−0·0006
Sept. 8, 1852.	Greenhithe		+0 5	+3 38	+0 27	+19 41	0·3368	− 2 37	−0·0456
Nov. 7, 1852.	*Rio Janeiro*		−0 10	+4 3	−0 9	+12 18	0·2130	− 1 52	−0·0326
Dec. 23, 1856.	Greenhithe		−0 11	+3 43	+0 10	+21 50	0·3719	− 3 26	−0·0599
May 1857.	*Ascension Island*		+1 3	+2 50	+1 21	+12 15	0·2122	− 4 2	−0·0703
November 1857.	*Cape of Good Hope*		−0 22	+2 55	−0 6	+16 27	0·2832	− 1 35	−0·0276
Oct. 31, 1859.	Greenhithe		−0 8	+3 26	+0 34	+18 40	0·3201	+ 0 50	0·0145
Nov. 19, 1855.	Greenhithe	HESPER, 808	+1 13	+3 10	+0 36	− 0 7	−0·0020	− 3 17	−0·0573
Oct. 11, 1856.	Greenhithe		+0 12	+3 0	+0 38	+ 1 28	0·0256	− 0 27	−0·0078
May 1, 1857.	Greenhithe		+0 12	+3 17	+0 21	+ 2 22	0·0413	+ 0 23	0·0067
June 8, 1848.	Greenhithe	CARADOC, 676	+0 43	+3 13	+0 18	−12 33	−0·2173	− 4 15	−0·0741
May 21, 1852.	*Malta*		+0 31	+2 15	−0 17	− 9 42	−0·1685	− 1 33	−0·0270
Nov. 4, 1855.	Greenhithe		−0 25	+2 6	+0 12	−10 54	−0·1891	− 2 8	−0·0372

TABLE I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Resultant of B and C, or ship's total force.		Magnetic elements.		Position of standard compass.			Beams.	Horse-power and engines.	Where built.	Date of launching.
Direction.	Amount.	Horizontal force.	Dip. and nat. tang.	From funnel.	From taffrail.	Height from deck.				
				ft. in.	ft. in.	ft. in.				
155°	0·146	1·000	+68° 30′ 2·54	26 4	49 8	5 2	Wood, on poop-deck.	350, Screw.	Blackwall (Ditchburn and Mare).	27th Jan. 1849.
143	0·111	1·000	+68 30 2·54	26 4	49 8	5 2				
111	0·093	1·000	+68 30 2·54	26 4	49 8	5 2				
81	0·092	1·000	+68 30 2·54	26 4	49 8	5 2				
114	0·183	1·000	+68 30 2·54	26 5	50 4	5 4				
100	0·166	1·000	+68 30 2·54	26 5	50 4	5 4				
189½	0·223	1·000	+68 30 2·54	78 4	38 0	3 9	Wood, on poop-deck.	350, Screw.	Millwall (Fairbairn).	22nd May, 1849.
193½	0·232	1·000	+68 30 2·54	78 4	38 0	3 9				
150	0·238	1·000	+68 30 2·54	78 4	38 0	3 9				
145	0·122 0·213	1·746	+50 0 1·19	78 4	38 0	3 9				
162	0·219	1·000	+68 30 2·54	77 0	39 0	4 0				
205	0·264	1·000	+68 45 2·57	52 0	38 0	4 1	Wood, on poop-deck.	556, Paddle.	Birkenhead (Laird).	30th Dec. 1845.
206	0·265	1·000	+68 45 2·57	52 0	38 0	4 1				
206	0·260	1·000	+68 45 2·57	52 0	38 0	4 1				
207	0·264	1·000	+68 45 2·57	52 0	38 0	4 1				
206	0·267	1·000	+68 45 2·57	52 0	38 0	4 1				
3	0·345	1·000	+68 45 2·57	36 6	35 0	5 0	Wood, on quarter-deck. Iron in fore-part of ship.	350, Paddle.	Blackwall (Ditchburn and Mare).	16th Dec. 1845.
352	0·238 0·359	1·510	+52 0 1·28	36 6	35 0	5 0				
359½	0·359	1·000	+68 45 2·57	36 6	35 0	5 0				
360	0·316	1·000	+68 45 2·57	36 6	35 0	5 0				
352½	0·342	1·000	+68 45 2·57	36 6	35 0	5 0				
351	0·216 0·368	1·708	−11 21 − 0·20	36 6	35 0	5 0				
351	0·376	1·000	+68 30 2·54	36 6	35 0	5 1				
341½	0·223 0·373	1·673	+ 0 30 0·01	36 6	35 0	5 1				
354½	0·285 0·335	1·174	−54 42 − 1·41	36 6	35 0	5 1				
2½	0·390	1·000	+68 25 2·53	36 6	35 0	5 1				
272	0·057	1·000	+68 30 2·54	49 6†	102 0	11 1	Iron.	120, Screw.		
344	0·026	1·000	+68 30 2·54	49 6	102 0	11 1				
9	0·042	1·000	+68 30 2·54	49 6	102 0	11 1				
199	0·230	1·000	+68 40 2·56	60 0	40 0	7 0	Wood.	350, Paddle.	Blackwall (Ditchburn and Mare).	3rd July, 1847.
189	0·171 0·258	1·511	+52 0 1·28	60 0	40 0	7 0				
191	0·193	1·000	+68 30 2·54	60 0	40 0	7 0				

† Compass before the funnel, on bridge.

Table I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients. A.	Permanent coefficients. D.	Permanent coefficients. E.	Coefficient B.	Ship's force to Head. Earth's horizontal force =1·000.	Coefficient C.	Ship's force to Starboard. Earth's horizontal force =1·000.
April 21, 1857.	*Malta*	Caradoc, 676..... *continued.*	+° 49′	+° 13′	+° 10′	− 8 36	−0·1495	− 1 38	−0·0285
Dec. 13, 1858.	*Malta*		+1 27	+2 52	−0 20	− 8 38	−0·1501	− 3 6	−0·0541
Sept. 8, 1847.	Greenhithe	Antelope, 650.....	+0 14	+2 58	+0 10	− 6 43	−0·1167	+ 0 59	0·0172
Mar. 24, 1852.	Greenhithe		+0 2	+2 30	+0 45	− 6 46	−0·1178	− 1 1	−0·0177
Sept. 8, 1853.	Portsmouth		−0 22	+2 19	+0 17	− 8 23	−0·1460	− 3 41	−0·0642
Jan. 8, 1857.	Greenhithe		+0 29	+3 4	+0 23	− 3 8	−0·0547	− 5 18	−0·0924
Mar. 1, 1848.	Greenhithe	Triton, 654.....	+0 40	+4 2	+0 32	−11 56	−0·2068	+ 0 26	0·0076
June 23, 1852.	Greenhithe		−0 3	+3 8	+0 23	− 7 47	−0·1354	− 2 32	−0·0442
Sept. 18, 1852.	*Corfu*		+1 10	+3 20	−0 2	− 5 36	−0·0976	− 2 4	−0·0361
Nov. 12, 1857.	Greenhithe		+0 25	+2 37	+0 39	− 8 37	−0·1498	− 5 34	−0·0970
Dec. 3, 1858.	*Fernando Po*		−1 0	+3 21	−0 5	− 5 36	−0·0976	− 0 4	−0·0012
Nov. 16, 1847.	Portsmouth	Oberon, 649.....	+1 35	+3 23	+0 13	+ 6 18	0·1097	−14 2	−0·2425
July 26, 1851.	Portsmouth		−0 20	+2 16	+0 20	+ 5 43	0·0996	−11 57	−0·2071
Nov. 28, 1856.	*Malta*		0 0	+2 43	−0 27	+ 3 27	0·0602	− 6 47	−0·1181
Aug. 10, 1858.	Greenhithe		−0 5	+3 27	+0 8	+ 8 15	0·1435	− 6 16	−0·1092
Dec. 30, 1858.	*Monte Video*		+2 11	+2 50	−0 38	+ 3 29	0·0602	− 5 23	−0·0938
July 19, 1854.	Greenhithe	Industry, 638.....	−0 34	+2 55	−0 32	+13 55	0·2405	+ 3 12	0·0558
Jan. 10, 1856.	*Malta*		−1 10	+3 0	−0 23	+ 9 9	0·1590	− 0 9	−0·0026
Sept. 30, 1856.	Greenhithe		−0 45	+2 45	−0 23	+14 27	0·2495	+ 3 13	0·0561
Jan. 13, 1858.	Greenhithe		+0 26	+2 31	+0 22	+13 17	0·2298	− 0 37	−0·0107
Aug. 25, 1858.	Greenhithe		+0 18	+2 23	−0 9	+10 25	0·1808	− 1 11	−0·0206
July 19, 1859.	Greenhithe		+0 13	+2 40	−0 13	+10 43	0·1859	+ 0 4	0·0011
Sept. 4, 1854.	Greenhithe*	Supply, 638.....	+0 29	+3 40	−0 4	−16 41	−0·2871	+12 2	0·2085
April 19, 1859.	Greenhithe		−0 10	+3 7	−0 3	−15 1	−0·2591	− 0 36	−0·0105
Sept. 19, 1859.	Greenhithe		−0 35	+2 23	−1 20	−14 3	−0·2428	− 0 53	−0·0154
Jan. 14, 1860.	Greenhithe		+0 41	+2 15	−0 47	−15 13	−0·2625	− 0 5	−0·0014
Mar. 30, 1855.	Plymouth	Weser†, 590.....	−0 07	+3 50	−0 39	−11 59	−0·2076	+ 1 16	0·0221
July 28, 1857.	*St. Geo. Mouth, R. Danube*		+0 9	+4 11	+0 38	− 6 33	−0·1141	− 4 47	−0·0834
Nov. 17, 1859.	Greenhithe		+0 9	+3 35	+0 23	+ 1 0	0·0174	+ 3 52	0·0674
Mar. 29, 1855.	Plymouth	Recruit† (Steam-vessel), 590.	+0 1	+4 7	−0 16	−13 47	−0·2382	− 0 53	−0·0154

* These observations were made with a common prismatic compass: the coefficients have been computed both directly from the observations, and from a probable curve graphically drawn through the observations: the results accord closely.

† These vessels were received from the Prussian Government in 1854.

TABLE I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Resultant of B and C, or ship's Total force.		Magnetic elements.		Position of standard compass.			Beams.	Horse-power and engines.	Where built.	Date of launching.
Direction.	Amount.	Horizontal force.	Dip, and nat. tang.	From funnel.	From taffrail.	Height from deck.				
				ft. in.	ft. in.	ft. in.				
191°	0·122 0·229	1·510	+53° 0 1·28	60 0	40 0	7 0	Wood.	350, Paddle.	Blackwall (Ditchburn and Mare).	July 3, 1847.
200	0·160 0·242	1·510	+53° 0 1·28	60 0	40 0	7 0				
171½	0·118	1·000	+68° 40 2·56	56 0	21 0	4 7½	Wood.	260, Paddle.	Blackwall (Ditchburn and Mare).	July 25, 1846.
188½	0·119	1·000	+68° 40 2·56	56 0	21 0	4 7½				
203½	0·161	1·000	+68° 40 2·56	56 0	21 0	4 7½				
239	0·106	1·000	+68° 40 2·56	37 0	41 0	4 8				
178	0·207	1·000	+68° 40 2·56	32 8	40 7	4 9	Wood.	260, Paddle.	Blackwall (Wigram).	Oct. 24, 1846.
198	0·142	1·000	+68° 40 2·56	32 8	40 7	4 9				
200	0·104 0·142	1·366	+55° 30 1·46	32 8	40 7	4 9				
213	0·178	1·000	+68° 25 2·53	35 0	36 0	4 9				
181	0·098 0·188	1·923	0 0	35 0	36 0	4 9				
294	0·266	1·000	+68° 40 2·56	52 4	21 2	4 9½	Wood.	260, Paddle.	Deptford (Rennie).	January 2, 1847.
295	0·230	1·000	+68° 40 2·56	52 4	21 2	4 9½				
297	0·133 0·201	1·510	+52° 0 1·28	52 4	21 2	4 9½				
323	0·180	1·000	+68° 30 2·54	41 10	30 3	4 10				
303	0·112 0·179	1·602	−32° 0 0·62	41 10	30 3	4 10				
13	0·247	1·000	+68° 25 2·53	73 5	18 11	4 11	Iron.	80, Screw.	Blackwall (Mare and Co.).	1854.
359	0·159 0·240	1·510	+52° 0 1·28	73 5	18 11	4 11				
13	0·256	1·000	+68° 25 2·53	73 5	18 11	4 11				
357½	0·230	1·000	+68° 25 2·53	73 5	18 11	4 11				
353½	0·182	1·000	+68° 25 2·53	73 5	18 11	4 11				
360½	0·186	1·000	+68° 25 2·53	73 5	18 11	4 11				
144	0·354	1·000	+68° 25 2·53	70 0	18 0	5 0	Iron.	80, Screw.	Blackwall (Mare and Co.).	June 3, 1854.
182	0·259	1·000	+68° 25 2·53	69 6	18 2	5 2				
183½	0·243	1·000	+68° 25 2·53	69 6	18 2	5 2				
180½	0·262	1·000	+68° 25 2·53	69 6	18 2	5 2				
174	0·209	1·000	+68° 30 2·54	8 10‡	66 0	11 7	Wood.	160, Paddle.		
216	0·141 0·173	1·230	+60° 0 1·73	8 10‡	66 0	11 7				
75½	0·069	1·000	+68° 25 2·53	42 4	30 0	4 6½				
184½	0·239	1·000	+68° 25 2·53	8 10‡	66 0	11 7	Wood.	160, Paddle.		

‡ Compass placed on the bridge, nearly midway between two funnels: the distance is given from the nearest funnel.

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Table I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients. A.	Permanent coefficients. D.	Permanent coefficients. E.	Coefficient B.	Ship's force to Head. Earth's horizontal force = 1·000.	Coefficient C.	Ship's force to Starboard. Earth's horizontal force = 1·000.
April 26, 1848.	Portsmouth	Sharpshooter, 503...	−0° 7′	+4° 32′	+0° 14′	− 7 17	−0·1268	+ 0 24	0·0070
		Heeled 7° to starboard.	+0 3	+4 13	−0 28	− 7 52	−0·1369	− 0 23	−0·0067
April 1, 1850.	Portsmouth		+0 16	+3 53	+0 5	− 6 1	−0·1048	+ 0 2	0·0006
Nov. 12, 1852.	Portsmouth		−0 33	+3 17	−0 21	−16 17	−0·2804	− 0 5	−0·0014
Feb. 8, 1853.	*Rio de Janeiro*		+0 20	+3 2	−0 2	− 8 25	−0·1464	− 1 25	−0·0247
Dec. 28, 1857.	*Portsmouth*		+0 10	+4 12	+0 3	−12 44	−0·2204	+ 4 40	0·0814
Aug. 31, 1859.	*Isles de Los, Africa*		−0 45	+3 35	+1 7	− 6 58	−0·1213	+ 0 56	0·0163
Aug. 28, 1846.	Greenhithe	Recruit (Sailing Brig), 462.	−0 30	+1 30	−0 33	+ 3 7	0·0544	+ 6 36	0·1149
Aug. 28, 1846.	Greenhithe		−0 41	+1 7	−1 3	+12 50	0·2221	+ 5 12	0·0906
Nov. 1846.	Plymouth	Heeled 8° to port	+2 18	+1 57	−0 8	+12 48	0·2215	+ 1 30	0·0262
		Heeled 8° to starboard.	+1 51	+2 19	−0 40	+12 41	0·2196	+ 7 27	0·1297
			+0 21	+2 5	−0 13	+14 10	0·2447	+14 25	0·2490
Oct. 18, 1855.	Greenhithe	Baron von Humboldt, *afterwards named*	−0 18	+5 10	+0 24	+16 33	0·2848	− 5 47	−0·1008
Dec. 15, 1855.	Greenhithe	Buffalo, 440	+0 3	+3 4	+0 5	−16 46	−0·2885	+ 0 35	0·0102
Dec. 24, 1856.	Greenhithe		+0 2	+3 2	+0 6	−19 6	−0·3272	− 0 47	−0·0137
Feb. 26, 1858.	Greenhithe		+0 39	+2 35	+0 23	+13 12	0·2283	+ 1 33	0·0270
Mar. 17, 1846.	Greenhithe	Myrmidon, 374	−0 16	+3 23	+0 3	+15 18	0·2639	+ 2 58	0·0517
Aug. 11, 1851.	Woolwich		+0 46	+3 9	−0 28	+19 23	0·3319	− 5 31	−0·0961
July 2, 1855.	Portsmouth		+0 21	+2 45	+0 12	+17 7	0·2943	+ 0 28	0·0081
Sept. 8, 1855.	Portsmouth	Wye, 700	+0 7	+3 24	+0 41	− 1 40	−0·0291	+12 53	0·2230
Sept. 6, 1845.	Plymouth	Bloodhound, 378	+0 23	+3 40	+0 10	+14 37	0·2523	− 2 12	−0·0384
1846.	*Constantinople*		+0 7	+3 22	−0 51	+10 40	0·1851	− 2 31	−0·0439
1846.	*Athens* (*Piræus*)		+0 25	+3 59	−0 6	+ 9 0	0·1564	− 2 32	−0·0442
May 11, 1847.	Greenhithe	Heeled 8° to port	+0 5	+3 21	+0 4	+11 43	0·2031	− 4 40	−0·0814
		Heeled 8° to starboard.	+0 32	+3 5	+0 20	+11 57	0·2071	− 1 48	−0·0314
			−0 17	+2 45	−0 20	+11 33	0·2002	+ 1 15	0·0218
Feb. 12, 1851.	Plymouth		−2 39	+2 35	+0 4	+12 20	0·2136	− 2 49	−0·0491
Sept. 7, 1855.	Greenhithe		+0 13	+2 31	+0 26	+11 46	0·2039	− 2 7	−0·0369
Mar. 20, 1845.	Greenhithe	Jackal, 340	−0 25	+4 57	−0 25	+24 7	0·4086	+ 0 45	0·0131
July 16, 1845.	Plymouth		+0 15	+4 13	−0 5	+16 38	0·2862	− 1 52	−0·0326
1846.	*Athens* (*Piræus*)		+0 15	+3 52	−0 7	+10 15	0·1779	− 0 47	−0·0137

TABLE I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Resultant of B and C, or ship's Total force.		Magnetic elements.		Position of standard compass.			Beams.	Horse-power and engines.	Where built.	Date of launching.
Direction.	Amount.	Horizontal force.	Dip, and nat. tang.	From funnel.	From taffrail.	Height from deck.				
			°	ft. in.	ft. in.	ft. in.				
17¾	0·196	1·000	+68 25	43 6	44 6	4 8½	Wood.	202, Screw.	Blackwall (Ditchburn and Mare).	July 25, 1846.
183	0·137		2·53	43 6	44 6	4 8½				
180	0·105	1·000	+68 25	46 0	43 0	4 8½				
180	0·280	1·000	2·53 +68 25	57 4	28 11	5 8				
189	0·142	1·708	2·53 −11 21	57 4	28 11	5 8				
	0·253		− 0·20							
160	0·235	1·000	+68 25	57 4	28 11	6 2				
172	0·122	1·821	2·53 +33 30	57 4	28 11	6 2				
	0·222		1·51							
65	0·127	1·000	+68 25		9 2		Wood beams. Iron bulwarks.	*Sailing vessel.*	Blackwall (Ditchburn and Mare).	1846.
22	0·240	1·000	2·53 +68 25		16 4					
7	0·223		2·53			1 7†				
30½	0·255	1·000	+68 25		16 4	8 10‡				
46	0·349		2·53							
339	0·302	1·000	+68 25	44 0	12 0	4 8	Iron.	60, Screw.		
178	0·289	1·000	2·53 +68 25	6 6*	63 0	11 0				
182	0·328	1·000	2·53 +68 25	6 6*	63 0	11 0				
7	0·230	1·000	2·53 +68 25	34 0	26 0	4 9				
			2·53							
11	0·269	1·000	+68 30	37 6	23 8	5 6	Iron.	150, Screw.	Blackwall (Ditchburn and Mare).	February 1845.
344	0·346	1·000	2·54 +68 30	37 6	23 8	5 6				
1½	0·294	1·000	2·54 +68 30	37 6	23 8	5 6				
			2·54							
97½	0·226	1·000	+68 30	51 3	47 8	4 4	Iron.	Screw.		
			2·54							
351	0·256	1·000	+68 40	41 6	14 0	5 6	Iron.	150, Paddle.	Glasgow (R. Napier).	9th Jan. 1845.
347	0·190	1·482	2·56 +54 0	41 6	14 0	5 6				
	0·281		1·38							
344	0·162	1·000	+68 40	41 6	14 0	5 6				
	0·249		2·56							
338	0·219			41 6	14 0	5 6				
351	0·209	1·000	+68 40	41 6	14 0	5 6				
6	0·202		2·56	41 6	14 0	5 6				
347	0·219	1·000	+68 40	42 3	15 10	5 6				
350	0·207	1·000	2·56 +68 40	42 3	15 10	5 6				
			2·56							
2	0·409	1·000	+68 40	25 6	32 6	7 0	Iron.	150, Paddle.	Glasgow (R. Napier).	28th Oct. 1844.
353	0·288	1·000	2·56 +68 40	42 2	16 8	7 0				
355½	0·178	1·539	2·56 +51 0	42 2	16 8	7 0				
	0·274		1·23							

* In these examples the compass was placed on the bridge *before* the funnel.

† Above the level of iron bulwarks.

‡ Distance from iron bulwarks.

Table I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients.			Coefficient	Ship's force to Head. Earth's horizontal force =1·000.	Coefficient	Ship's force to Starboard. Earth's horizontal force =1·000.
			A.	D.	E.	B.		C.	
1847.	*River Tagus*	JACKAL, 340 *continued.*	−0° 13′	+4° 2′	+0° 22′	+12° 15′	0·2122	− 1° 39′	−0·0283
Jan. 26, 1849.	Portsmouth		+0 18	+2 58	+0 38	+14 49	0·2557	− 4 12	−0·0732
Aug. 5, 1854.	Greenhithe		+0 10	+3 8	−0 35	+15 38	0·2695	− 9 31	−0·1653
May 10, 1859.	Greenhithe		+0 25	+3 1	+0 33	+14 10	0·2447	− 5 29	−0·0955
Jan. 30, 1846.	Greenhithe	HARPY, 343	−0 15	+2 54	+0 48	+ 7 3	0·1297	+ 2 19	0·0404
May 1, 1854.	Falmouth		−1 2	+2 41	−0 30	+ 8 43	0·1515	+ 0 49	0·0143
Dec. 23, 1857.	*Malta*		−0 15	+2 50	−0 18	+ 6 14	0·1086	− 0 53	−0·0154
Mar. 6, 1860.	Greenhithe		+0 48	+2 32	−0 4	+11 12	0·1942	− 1 25	−0·0247
1845.	Greenhithe	LIZARD, 340	−0 3	+3 49	+0 19	+13 31	0·2337	− 2 3	−0·0358
April 7, 1853.	Sheerness		+0 34	+2 59	+0 53	+10 49	0·1877	+ 0 36	0·0105
Feb. 8, 1858.	Sheerness		+0 23	+3 4	+0 22	+ 9 51	0·1711	+ 0 52	0·0151
Aug. 24, 1847.	Portsmouth	FIREQUEEN, 313	−0 5	+3 27	−0 21	+ 9 14	0·1605	− 7 47	−0·1354
Nov. 8, 1852.	Portsmouth		−0 3	+2 53	−0 37	+ 9 48	0·1702	− 5 47	−0·1008
June 5, 1858.	Portsmouth		+0 17	+2 14	+0 8	+ 4 49	0·0840	+ 0 51	0·0148
July 8, 1845.	Greenhithe	FAIRY (*Yacht*), 312	+0 3	+1 58	−0 17	+ 3 55	0·0683	+ 1 3	0·0183
Mar. 22, 1849.	Portsmouth		+0 35	+2 8	+0 22	− 7 46	−0·1351	− 0 32	−0·0093
Feb. 19, 1850.	Portsmouth		+0 5	+1 50	+0 30	− 4 20	−0·0756	− 1 16	−0·0221
			+0 35	+3 33	+0 31	+13 25	0·2320	− 1 15	−0·0218
June 19, 1852.	Portsmouth		−0 33	+3 23	+0 6	+11 39	0·2019	− 0 33	−0·0096
Jan. 23, 1858.	Portsmouth		−0 20	+3 11	−0 22	+11 23	0·1974	+ 2 2	0·0355
June 5, 1854.	Greenhithe	MINX, 303	+0 15	+3 7	−0 6	− 1 54	−0·0331	− 2 20	−0·0407
Oct. 14, 1859.	Greenhithe	*	+1 37	+4 29	+0 15	− 4 48	−0·0837	− 4 11	−0·0729
1846.	Greenhithe	ONYX, 297	−0 18	+3 42	−0 24	− 7 54	−0·1374	− 4 16	−0·0744
1848.	Greenhithe		+0 25	+3 36	+0 25	− 5 30	−0·0958	− 3 53	−0·0677
1850.	Greenhithe	†	+0 39	+3 26	+0 27	+ 2 19	0·0404	− 8 23	−0·1458
Dec. 20, 1844.	Greenhithe	PRINCESS ALICE, 270	+0 21	+3 1	+0 10	+14 54	0·2571	+ 0 24	0·0070
Dec. 26, 1850.	Greenhithe		−0 7	+2 55	0 0	+12 59	0·2247	− 0 19	−0·0055
April 15, 1855.	Sheerness		+2 3	+3 36	−0 13	+12 1	0·2082	− 2 35	−0·0451
July 26, 1856.	Greenhithe		−0 12	+2 32	+0 16	+10 5	0·1751	− 1 47	−0·0311
May 18, 1859.	Greenhithe	BANN, 267	−2 15	+4 15	−0 39	+15 6	0·2605	+14 46	0·2549

* Fitted with iron tanks nearly the entire length of the vessel, for the purpose of carrying water.

† After a thorough repair, new boilers and funnel, and Standard compass placed 6 inches further forward.

Table I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Resultant of B and C, or ship's Total force.		Magnetic elements.		Position of standard compass.			Beams.	Horse-power and engines.	Where built.	Date of launching.
Direction.	Amount.	Horizontal force.	Dip, and nat. tang.	From funnel.	From taffrail.	Height from deck.				
				ft. in.	ft. in.	ft. in.				
35½°	0·214	1·217	+63° 0	42 2	16 8	7 0	Iron.	150, Paddle.	Glasgow (R. Napier).	28th October, 1844.
	0·260		1·96							
344	0·266	1·000	+68 40	42 2	16 8	7 0				
			2·56							
328½	0·316	1·000	+68 25	41 0	15 0	5 5				
			2·53							
339	0·262	1·000	+68 25	41 0	15 0	5 5				
			2·53							
18	0·129	1·000	+68 25	43 0	14 0	5 3	Wood, on quarter-deck.	200, Paddle.	Blackwall (Ditchburn and Mare).	March, 1845.
			2·53							
6	0·152	1·000	+68 25	43 0	14 0	4 10				
			2·53							
35½	0·110	1·510	+52 0	43 0	14 0	4 10				
	0·166		1·28							
353	0·196	1·000	+68 25	43 0	14 0	4 10				
			2·53							
351	0·236	1·000	+68 40	41 9	15 1	5 0	Iron.	150, Paddle.	Glasgow (R. Napier).	28th November, 1844.
			2·56							
3	0·188	1·000	+68 40	41 9	15 1	5 0				
			2·56							
5	0·172	1·000	+68 40	41 9	15 1	5 0				
			2·56							
320	0·210	1·000	+68 30	55 0	31 9			120, Paddle.		Purchased July 1847.
			2·54							
329½	0·197	1·000	+68 30	55 0	31 9					
			2·54							
10	0·085	1·000	+68 30	62 9	25 0	3 7				
			2·54							
15	0·070	1·000	+68 30	unknown.			Wood.	120, Screw.	Blackwall (Ditchburn and Mare).	March, 1845.
			2·54							
184	0·135	1·000	+68 30	52 0	15 0	2 9½				
			2·54							
196	0·079	1·000	+68 30	48 10	15 2	2 9				
			2·54							
355	0·233	1·000	+68 30	26 0	39 0	2 8				
			2·54							
357	0·202	1·000	+68 30	26 0	39 0	2 8				
			2·54							
10	0·201	1·000	+68 30	26 0	39 0	2 8				
			2·54							
231	0·052	1·000	+68 30	18 0	18 0	5 0		100, Screw.	Blackwall (Wigram).	5th September, 1846.
			2·54							
221	0·111	1·000	+68 30	36 0	9 6	3 6				
			2·54							
209	0·157	1·000	+68 30	23 0				120, Paddle.	Blackwall (Ditchburn and Mare).	November. 1845,
			2·54							
215	0·117	1·000	+68 30	23 0						
			2·54							
285	0·151	1·000	+68 30	22 6						
			2·54							
2	0·257	1·000	+68 30	22 0	35 6	5 10	Wood.	120, Paddle.	Blackwall.	1843.
			2·54							
358	0·225	1·000	+68 30	22 0	35 6	5 10				
			2·54							
348	0·213	1·000	+68 30	22 0	35 6	5 10				
			2·54							
350	0·178	1·000	+68 30	26 5	34 0	5 10				
			2·54							
44½	0·364	1·000	+68 30	49 0	29 0	4 7	Iron.	80, Paddle.	Millwall (J. S. Russell).	5th July, 1856.
			2·54							

Table I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients. A.	D.	E.	Coefficient B.	Ship's force to Head. Earth's horizontal force =1·000.	Coefficient C.	Ship's force to Starboard. Earth's horizontal force =1·000.
May 25, 1857.	Sheerness	Brune, 267	−0° 35′	+0° 22′	+0° 56′	− 9′ 15″	−0·1607	+ 3′ 28″	0·0605
Aug. 7, 1849.	*Penetanguishine, Lake Huron, Canada.*	Mohawk, 228	−1 28	+3 1	−1 47	+10 15	0·1779	− 8 5	−0·1406
1846.	Greenhithe	Torch, 343	−0 26	+2 56	+0 5	+11 8	0·1931	− 4 3	−0·0706
May 10, 1852.	Greenhithe		−0 4	+2 43	+0 24	+10 41	0·1854	− 0 46	−0·0134
July 6, 1852.	*Madeira*		+3 2	+2 52	−0 5	+ 6 25	0·1117	− 1 20	−0·0233
			+2 48	+2 10	−0 43	+ 6 52	0·1196	− 0 57	−0·0166
July 22, 1852.	*St. Vincent, Cape de Verd Islands.*		−1 40	+2 46	−0 52	+ 7 4	0·1230	− 1 10	−0·0204
Sept. 29, 1852.	*Rio de Janeiro*		−0 7	+2 29	+0 9	+ 7 17	0·1268	− 1 6	−0·0192
Nov. 16, 1852.	*Tristan d'Acunha*		+0 12	+2 23	−0 56	+ 7 42	0·1340	− 3 13	−0·0561
Dec. 10, 1852.	*Cape of Good Hope*		−1 17	+1 57	+0 6	+ 9 18	0·1616	+ 0 30	0·0087
Jan. 26, 1853.	*St. Paul's Island, Indian Ocean.*		+1 58	+1 39	+0 6	+10 17	0·1785	− 0 28	−0·0081
Feb. 18, 1853.	*Swan River, Australia*		−1 5	+1 31	−0 15	+ 6 58	0·1213	− 0 13	−0·0038
Mar. 15, 1853.	*King George's Sound*		−2 8	+2 44	+0 44	+ 8 41	0·1510	− 1 13	−0·0212
July 1856.	*East Coast, Australia*		+0 25	+1 37	−0 11	+ 8 18	0·1443	+ 0 23	0·0067
May 11, 1844.	Woolwich	Dover, 224	+1 14	+2 38	+0 8	− 6 57	−0·1210	− 4 10	−0·0727
Sept. 25, 1849.	Plymouth		+0 2	+2 23	−0 18	− 4 58	−0·0866	+ 0 25	0·0073
June 23, 1843.	Greenhithe	Wilberforce, 457	+0 33	+2 18	+0 15	− 7 48	−0·1357	− 7 15	−0·1262
July 5, 1843.	*River Gambia*		0 0	+2 6	+0 7	− 4 39	−0·0811	− 4 12	−0·0732
Jan. 13, 1844.	Greenhithe	Dwarf, 164	−0 35	+2 2	+0 17	+13 5	0·2264	− 3 8	−0·0547

Table II.—Floating Batteries*, Her Majesty's Navy.

July 1857.	Sheerness	Terror, 1971	−1 45	+6 17	−0 44	+25 12	0·4258	+2 3	0·0358
July 5, 1855.	Greenhithe	Meteor	−1 19	+0 12	0 0	− 1 19	−0·0230	−3 31	−0·0613
Mar. 31, 1856.	Sheerness	Thunder, 1469	+0 34	−0 40	+0 9	−11 33	−0·2002	−1 33	−0·0270
Mar. 26, 1856.	Sheerness	Trusty, 1539	+0 4	+1 37	−1 54	−16 55	−0·2910	+3 52	0·0674

* Of these, Terror is the only *Iron-built* vessel; the others are *Wood-built* plated with iron.

TABLE I.—Iron-built Ships, Her Majesty's Navy (*continued*).

Resultant of B and C, or ship's Total force.		Magnetic elements.		Position of standard compass.			Beams.	Horse-power and engines.	Where built.	Date of launching.
Direction.	Amount.	Horizontal force.	Dip, and nat. tang.	From funnel.	From taffrail.	Height from deck.				
°			° ′	ft. in.	ft. in.	ft. in.				
159½	0·171	1·000	+68 30 2·54	45 3	28 8	4 4	Iron.	80, Paddle.	Millwall (J. S. Russell).	30th August, 1856.
321	0·227	0·876	+76 0 4·01	10 0				60, Paddle.	Limehouse (Fairbairn and Co.).	Kingston, Upper Canada. 21st Feb. 1843†.
340	0·206	1·000	+68 40 2·56	42 0	16 0	6 0	Iron.	150, Paddle.	Blackwall (Ditchburn and Mare).	February, 1845.
356	0·186	1·000	+68 40 2·56	42 0	16 0	5 7				
34⅜	0·114 0·153	1·339	+60 40 1·78	42 0	16 0	5 7				
352	0·120 0·161	1·339	+60 40 1·78	42 0	16 0	5 7				
350½	0·125 0·198	1·585	+46 0 1·04	42 0	16 0	5 7				
351½	0·123 0·219	1·709	−11 21 −0·20	42 0	16 0	5 7				
337	0·146 0·189	1·295	−43 0 −0·93	42 0	16 0	5 7				
3	0·162 0·190	1·174	−54 42 −1·41	42 0	16 0	5 7				
357	0·179 0·198	1·106	−68 0 −2·48	42 0	16 0	5 7				
358	0·122 0·182	1·490	−62 30 −1·92	42 0	16 0	5 7				
352	0·152 0·214	1·406	−65 0 −2·14	42 0	16 0	5 7				
3	0·145 0·246	1·7 approx.		42 0	16 0	5 7				
211	0·141	1·000	+68 40 2·05		unknown.		Iron.	100, Paddle.	Liverpool (Laird).	1840.
175	0·087	1·000								
223	0·185	1·000	+68 40 2·56	unknown.		7 0	Iron.	100, Paddle.	Liverpool.	1841.
222	0·109 0·193	1·771	+38 30 0·79							
346	0·233	1·000	+68 40 2·56	32 9	unknown.		Wood.	90	Blackwall.	1842.

TABLE II.—Floating Batteries, Her Majesty's Navy (*continued*).

5	0·426	1·000	+68 25 2·53	70 0	37 0	5 5	Iron.	Screw.	Newcastle-on-Tyne (Palmer).	26th April, 1856.
249	0·065	1·000	+68 25 2·53	79 0	16 6	4 8	Wood.	Screw.		
188	0·202	1·000	+68 25 2·53	83 0	10 10	4 7	Wood.	Screw.		
167	0·299	1·000	+68 25 2·53	84 0	9 10	4 6	Wood.	Screw.		

† Delivered in parts at Woolwich, November 1841.

Table III.—Screw Steam-vessels, Her Majesty's Navy (Wood-built).

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients.			Coefficient	Ship's force to Head. Earth's horizontal force =1·000.
			A.	D.	E.	B.	
April 29, 1859.	Portsmouth	Mersey, 3739	+0° 52′	−0° 15′	−0° 5′	+7′ 44′	0·1346
Jan. 5, 1860.	Sheerness	Ariadne, 3202	+0 8	+0 31	−0 12	+ 8 37	0·1498
Mar. 29, 1859.	Plymouth	Doris, 2479	+1 11	−0 30	+0 43	+ 7 11	0·1250
Jan. 7, 1856.	Plymouth	Sanspareil, 2334	+0 4	+0 58	−0 13	+23 43	0·4022
May 22, 1857.	*Cape of Good Hope*		−0 37	+1 16	+0 36	+ 3 41	0·0642
1857.	*Canton*		+0 8	+0 53	−0 7	+ 7 41	0·1337
Oct. 20, 1859.	Portsmouth	Arrogant, 1872	−0 32	+0 20	+0 10	+ 6 21	0·1106
Sept. 5, 1859.	Sheerness	Clio, 1470	−0 43	+0 56	+0 4	+ 9 39	0·1676
June 1, 1859.	Sheerness	Cadmus, 1462	−0 23	−0 20	−0 4	+11 1	0·1911
June 7, 1856.	Portsmouth	Pylades, 1278	+1 22	+0 27	−1 6	+12 48	0·2215
Sept. 9, 1856.	*Sydney, C. Breton Island*		−0 6	0 0	−0 12	+17 47	0·3054
Sept. 26, 1856.	Portsmouth	Highflyer, 1161	+0 52	+0 36	+0 13	+11 42	0·2028
Dec. 12, 1856.	*Rio de Janeiro*		+1 4	−0 42	+0 7	+ 4 49	0·0840
Feb. 1857.	*Cape of Good Hope*		−0 50	−0 23	−0 8	+ 4 20	0·0755
May 26, 1857.	*Hong Kong*		+0 7	−0 32	+0 10	+ 3 21	0·0584
Dec. 2, 1857.	*Canton River*		+0 15	+0 6	+0 10	+ 3 45	0·0654
May 17, 1858.	*Shanghae*		−0 3	−0 5	+0 39	+ 6 25	0·1118
May 23, 1859.	Portsmouth	Falcon, 992	+0 15	+0 10	−0 25	+ 6 37	0·1152
1859.	Plymouth	Encounter, 953	+0 29	+0 27	−0 3	+ 7 1	0·1222
Nov. 28, 1859.	Greenhithe	Mutine, 875	+0 12	−0 19	−0 10	+ 8 35	0·1492
Nov. 19, 1859.	Sheerness	Fawn, 748	+0 16	+0 42	−0 40	+ 7 21	0·1279
May 21, 1857.	Plymouth	Cordelia, 579	+0 19	−0 40	−0 5	+ 7 57	0·1383
Aug. 8, 1857.	*Cape of Good Hope*		+1 5	+0 20	−0 22	− 1 12	−0·0209
Sept. 20, 1858.	*Apia, Upolu, Pacific Ocean*		−0 27	+0 40	+1 10	+ 1 24	0·0244
Mar. 7, 1857.	Portsmouth	Plumper, 490	+0 14	+0 52	+0 5	+ 6 1	0·1048
April 1857.	*Lisbon*		+0 4	−0 10	−0 18	+4 39	0·0811
May 1857.	*Rio de Janeiro*		−0 49	+0 47	+0 14	+ 2 8	0·0372
Sept. 1, 1857.	*Valparaiso*		+0 6	+0 37	+0 37	+ 1 6	0·0192
Oct. 1857.	*Sandwich Islands*		−0 49	+0 26	+0 5	+ 2 17	0·0398
Jan. 30, 1858.	*Vancouver I., Esquimalt*		−0 13	+0 23	−0 3	+ 5 45	0·1002
June 17, 1859.	*Vancouver I., Nanaimo*		+0 52	+0 5	+0 5	+ 6 26	0·1120
Jan. 1, 1856.	Greenhithe	Tickler (Gun-boat), 239	−1 37	+1 26	−0 13	+ 0 15	0·0043

TABLE III.—Screw Steam-vessels, Her Majesty's Navy (Wood-built) (*continued*).

Coefficient C.	Ship's force to Starboard. Earth's horizontal force =1·000.	Resultant of B and C, or ship's Total force. Direction.	Resultant of B and C, or ship's Total force. Amount.	Magnetic elements. Horizontal force.	Magnetic elements. Dip, and nat. tang.	Position of standard compass. From funnel.	Position of standard compass. Height from deck.	Horse-power of engines.
		°			° ′	ft. in.	ft. in.	
+1 23	0·0241	10	0·137	1·000	+68 15	121 0	7 10	1000
−2 26	−0·0424	344	0·156	1·000	+68 15	119 0	6 3	800
−1 15	−0·0218	350	0·127	1·000	+68 15	110 0	6 11	800
+1 45	0·0305	4½	0·404	1·000	+68 15 / 2·50	19 4	On poop.	400
+2 8	0·0372	30	0·074	1·174	−54 42 / − 1·41	19 4		
+0 57	0·0166	7	0·135	2·049	+31 30 / 0·61	19 4		
−0 28	−0·0081	356	0·111	1·000	+68 15 / 2·50	68 0	6 7	360
+4 46	0·0831	26½	0·187	1·000	+68 15 / 2·50	80 0	7 6	400
+2 35	0·0451	13	0·196	1·000	+68 15 / 2·50	87 0	6 6	400
+4 23	0·0764	19	0·234	1·000	+68 15 / 2·50			350
+5 22	0·0935	17	0·320	0·772	+76 30 / 4·17			
+0 48	0·0140	4	0·203	1·000	+68 15 / 2·50	70 0	6 0	250
+0 8	0·0023	2	0·084	1·708	−11 21 / − 0·20	70 0	6 0	
−1 18	−0·0227	343	0·079	1·174	−54 42 / − 1·41	70 0	6 0	
+0 29	0·0084	8	0·059	2·049	+31 26 / 0·61	70 0	6 0	
+0 9	0·0026	2	0·065	2·049	+32 35 / 0·63	70 0	6 0	
+0 20	0·0058	3	0·112	1·813	+45 18 / 1·01	70 0	6 0	
−2 39	−0·0462	338	0·124	1·000	+68 15 / 2·50	71 0	7 0	100
+0 10	0·0029	1	0·122	1·000	+68 15 / 2·50	73 0	5 5	360
−2 50	−0·0494	342	0·157	1·000	−68 15 / 2·50	70 0	6 6	200
−1 55	−0·0334	345½	0·132	1·000	+68 15 / 2·50	71 0	6 7	100
−0 27	−0·0078	357	0·139	1·000	+68 15 / 2·50	64 0	6 5	150
+1 40	0·0291	126	0·036	1·174	−54 42 / − 1·41	64 0	6 5	
−0 26	−0·0076	343	0·025	2·083	−35 30 / − 0·72	64 0	6 5	
+1 13	0·0212	11	0·107	1·000	+68 15 / 2·50	38 7	5 6	60
+1 8	0·0198	13	0·083	1·216	+61 5 / 1·81	38 7	5 6	
+0 32	0·0093	14	0·038	1·709	−11 21 / − 0·20	38 7	5 6	
+0 3	0·0008	2	0·019	1·887	−35 37 / − 0·72	38 7	5 6	
+0 20	0·0058	8	0·040	1·628	−42 00 / − 1·11	38 7	5 6	
+0 55	0·0160	9	0·102	1·040	+71 55 / 3·06	38 7	5 6	
+0 29	0·0084	5	0·112	1·016	+72 25 / 3·15	38 7	5 6	
−0 57	−0·0166	285	0·017	1·000	+68 15 / 2·50	35 0	3 7	60 high pressure

TABLE IV.—Paddle-wheel Steam-vessels, Her Majesty's Navy (Wood-built).

Date.	Place of observation.	Ship's name and Tonnage.	Permanent coefficients.			Coefficient	Ship's force to Head. Earth's horizontal force = 1·000.	Coefficient	Ship's force to Starboard. Earth's horizontal force = 1·000.	Resultant of B and C, or ship's Total force.		Magnetic elements.		Position of standard compass.		Horse-power of engines.
			A.	D.	E.	B.		C.		Direction.	Amount.	Horizontal force.	Dip, and nat. tang.	From funnel.	Height from deck.	
														ft. in.	ft. in.	
May 27, 1846.	Greenhithe ...	TERRIBLE, 1847.	−0° 12′	+0° 55′	+0° 8′	+5° 05′	0·0886	+0° 10′	0·0029	3° 2′	0·089	1·000	69° 0′ 2·60	33 9	.....	800
Dec. 26, 1845.	Sheerness	RETRIBUTION, 1641.	−0 48	+1 22	+0 7	+10 21	0·1797	+4 20	0·0755	23	0·195	1·000	+69 0 2·60	57 6	7 9	400
Oct. 8, 1856.	Sheerness		−1 7	+0 30	+0 20	+ 9 33	0·1659	+4 27	0·0776	25	0·183	1·000	+69 0 2·60			
Aug. 17, 1857.	*Callao*		−0 5	+0 13	+0 3	+ 2 59	0·0520	+0 49	0·0142	15	0·054	1·963	− 7 0 − 0·12			
Mar. 1859.	*Hong Kong* ...		+0 18	+0 12	−0 1	+ 4 29	0·0782	+1 16	0·0221	16	0·081	2·049	+31 26 0·61			
Sept. 1843.	.....	PENELOPE, 1616.	+0 17	+1 25	+0 21	+ 7 24	0·1288	+0 18	0·0052	2	0·129	1·000	69 0 2·60	35 0		
May 29, 1857.	Sheerness	CYCLOPS, 1106.	−0 15	+2 10	−0 1	+ 6 51	0·1193	−1 9	−0·0201	350	0·121	1·000	+68 30 2·53	38 6	4 3	320
Aug. 17, 1857.	*St. John's, Newfoundland.*		+0 23	+1 34	+0 36	+ 9 31	0·1653	−1 1	−0·0177	354	0·166	0·776	+76 0 4·01	38 6	4 3	
Dec. 1859.	*Kurrachee* ...		+0 16	+1 17	+0 24	+ 2 26	0·0424	−0 10	−0·0029	356	0·042	2·012	+28 15 0·54	38 6	4 3	
Sept. 5, 1848.	Portsmouth ...	SPHYNX, 1056.	+0 15	+1 50	−0 18	+ 8 58	0·1558	+0 23	0·0067	2	0·156	1·000	+69 0 2·60	32 3	.....	500
1851.	*Hong Kong* ...		−0 46	+0 35	−0 33	+ 2 34	0·0443	−0 12	−0·0035	356	0·045	2·049	+31 26 0·61	32 3		
1847.	Sheerness	GEYSER, 1054.	+0 2	+1 14	−0 4	+ 9 12	0·1599	−2 3	−0·0358	347	0·164	1·000	+69 0 2·60	33 0	.....	280
1850.	*C. of Good Hope*		−0 46	+0 59	+0 11	− 2 12	−0·0324	−0 56	−0·0163	203	0·042	1·174	−54 42 − 1·41			
Oct. 17, 1857.	Plymouth	STYX, 1057	+1 30	+1 37	+0 3	+ 5 33	0·0967	0 0	0·0000	360	0·097	1·000	+68 30 2·53	36 10	5 7	280
July 1859.	*Halifax, N.S.* ...		−1 27	+1 40	+0 8	+ 8 18	0·1443	+0 35	0·0102	4	0·145	0·823	+75 30 3·87			
1847.	Greenhithe ...	ACHERON, 720.	+0 23	+0 58	+0 3	+ 7 43	0·1343	+2 23	0·0416	17	0·141	1·000	+68 40 2·56	30 0	5 0	170
1850.	*Port Nicholson, New Zealand.*		+0 54	−0 33	−0 16	+ 1 26	0·0250	−1 47	−0·0311	309	0·040	1·382	−65 0 − 2·14			

TABLE V.—Steam-Ship *Great Eastern* (Iron-built).

Date.	Place of observation.	Vessel's name and Tonnage.	Permanent coefficients. A.	Permanent coefficients. D.	Permanent coefficients. E.	Coefficient B.	Ship's force to Head. Earth's horizontal force = 1·000.	Coefficient C.	Ship's force to Starboard. Earth's horizontal force = 1·000.	Resultant of B and C, or ship's Total force. Direction.	Resultant of B and C, or ship's Total force. Amount.	Position of compass.
							By Admiralty Standard Compasses.					
Sept. 7, 1859.	River Thames...	GREAT EASTERN, 22,000	−0° 10′	+4° 21′	−0° 37′	+23° 13′	0·3942	+25° 38′	0·4326	47°	0·585	Height from deck ..... ft. 4 in. 11
Sept. 10, 12, 1859.	Portland ...		−1 3	+4 44	−0 45	+22 42	0·3859	+16 43	0·2876	37	0·480	From rudder head 41 0
Oct. 22, 24, 1859.	Holyhead		−0 24	+4 8	−0 17	+19 18	0·3305	+12 3	0·2088	32	0·390	„ spindle of capstan 17 6
												„ nearest funnel ... 165 0
							Mast Compass, 45 feet from deck.					
Sept. 7, 1859.	River Thames...		+0 4	+1 32	+0 4	+12 43	0·2201	+11 12	0·1942	41	0·295	
Sept. 10, 12, 1859.	Portland		+1 21	+1 30	−0 10	+16 12	0·2790	+ 4 20	0·0756	15	0·290	
Oct. 22, 24, 1859.	Holyhead		+2 20	+1 0	+0 7	+17 2	0·2929	+ 7 30	0·1305	24	0·320	
							Platform Compass.					For relative positions, see Plate XV.
Sept. 7, 1859.	River Thames...		−1 40	+7 55	−0 12	+13 34	0·2346	+22 41	0·3856	59	0·455	
Sept. 10, 12, 1859.	Portland		+0 43	+5 19	+0 40	+10 17	0·1785	+21 5	0·3597	64	0·405	
							Foremost Bridge Compass.					
Sept. 7, 1859.	River Thames...		+0 3	+4 31	−0 9	+31 55	0·5287	+17 47	0·3054	30	0·610	

Supplement.

[*Added during the printing of the paper.*]

In June 1860, prior to the departure of the steam-ship Great Eastern on her first Atlantic voyage, I was enabled, through the attention and cooperation of the captain, John V. Hall, and managing director, T. Bold, Esq., to institute further experiments on the changes of the ship's magnetism, under the same conditions as those already recorded as having been made in the River Thames, at Portland, and at Holyhead, in September and October 1859.

Subsequent to the observations made at Holyhead, the Great Eastern rode out a violent gale in that harbour,—remarkable as causing the total wreck of the ship Royal Charter in the immediate neighbourhood,—which necessarily subjected many parts of the hull to severe concussion from the strain on the cables: the ship's services were then confined to the passage to Southampton; and during the sojourn at that port for the following seven months, she quietly swung round the moorings to the tides and variable winds. Extensive artificers' works were latterly performed in the internal equipments.

These details are worthy of notice, from the striking progressive diminution of the ship's magnetic force, and further tendency to the fore-and-aft direction of the neutral points of disturbance which the Southampton observations developed.

The same Admiralty standard compass having been placed in the exact position of former experiments, the correct magnetic bearing of the extreme point of the Isle of Wight, visible from the anchorage (distant 12 miles), was determined from a series of astronomical bearings and the known magnetic variation of the place, the necessary correction for parallax due to the length of the ship being allowed for the successive points of the compass as the ship swung round.

From the wind prevailing in one direction for several days prior to the departure of the Great Eastern, I was only able, although engaged on the 13th, 14th, and 15th of June, to obtain the deviations on sixteen and a half consecutive points; namely, from S.S.E., by the South, to N.N.W. ½ W.: these deviations, resulting from a curve drawn through fifty-one separate determinations, made under highly favourable circumstances, were as follows:—

Ship's head by Stand: comp:	Deviation.	Head by Stand: comp:	Deviation:	Head by Stand: comp:	Deviation.
S.S.E. . .	2° 0′ E.	S.W. . . .	6° 30′ W.	W.N.W. . .	14° 50′ W.
S. by E. . .	0 20 E.	S.W. by W. .	8 25 W.	N.W. by W.	14 15 W.
South . . .	1 40 W.	W.S.W. . .	10 15 W.	N.W. . . .	12 50 W.
S. by W. . .	3 40 W.	W. by S. . .	12 0 W.	N.W. by N.	10 10 W.
S.S.W. . .	4 45 W.	West . . .	13 0 W.	N.N.W. ½ W.	8 0 W.
S.W. by S. .	5 30 W.	W. by N. . .	14 20 W.		

It was necessary to deduce from these results the probable values for the remaining points of the compass; this appeared to be obtained with sufficient accuracy by trials of the coefficients B, C, D, with various assumed values, adopting those, the deviations resulting from which should approximate most closely to the actual observed deviations on the sixteen and a half determined points. The coefficients A and E were, under the circumstances, assumed as 0° 0′.

The resulting values for B of +13° 30′, C+1° 40′, D+4° 20′, afforded a satisfactory approximation; from whence the ship's force in direction and amount are respectively 7° and 0·235, the earth's horizontal magnetic force being considered, as at the other ports, 1·000.

A recapitulation of the Great Eastern's total magnetic force at each place of observation is herewith appended, as also a Table of deviations, which brings practically to view the change in the deviation of the mariners compass in a newly launched iron vessel, amounting in this special case to a decrease of 12° on some points of the compass in the first five days, 19° in seven weeks, and nearly three points, or 32° 10′ in the first nine months of service afloat.

	Angle of force from ship's head.	Total force.	Earth's horizontal force.
1859. September 7, River Thames . .	47°	0·585	1·000
„ „ 10—12, Portland . . .	37	0·480	„
„ Oct. 22—24, Holyhead . . .	32	0·390	„
1860. June 13—15, Southampton . .	7	0·235	„

Deviations

Deviations of the Compass observed on board the steam-ship *Great Eastern*, 1859–60; in a position on the upper deck, in the middle line of the ship; distant 46 feet 4 inches from the after or jigger mast; 17 feet 6 inches before the spindle of the after capstan, and 41 feet 0 inches before the rudder head; the needle elevated 4 feet 11 inches from the deck.

Ship's head, *correct* magnetic.	River Thames, 7th September, 1859.	Portland, 10th to 12th Sept. 1859.	Holyhead, 22 to 24th October, 1859.	Southampton, 13th, 14th, 15th June, 1860.
North.	15° 50′ E.	9° 20′ E.	7° 0′ E.	1° 15′ E.
N. by E.	21 0 „	14 40 „	10 50 „	4 30 „
N.N.E.	25 0 „	19 25 „	14 50 „	7 25 „
N.E. by N.	29 0 „	23 0 „	18 10 „	10 0 „
N.E.	32 0 „	26 30 „	21 20 „	12 40 „
N.E. by E.	36 0 „	29 20 „	24 0 „	14 50 „
E.N.E.	38 10 „	31 0 „	25 30 „	16 10 „
E. by N.	39 0 „	31 15 „	26 0 „	16 50 „
East.	38 0 „	30 10 „	25 0 „	16 0 „
E. by S.	32 30 „	26 0 „	22 0 „	14 0 „
E.S.E.	22 0 „	20 20 „	17 0 „	11 30 „
S.E. by E.	6 0 „	12 0 „	9 20 „	8 30 „
S.E.	10 30 W.	0 0 „	1 15 „	5 30 „
S.E. by S.	23 40 „	11 00 W.	5 40 W.	3 0 „
S.S.E.	29 30 „	17 40 „	10 50 „	2 40 „
S. by E.	31 20 „	21 30 „	14 20 „	0 20 „
South.	31 30 „	23 0 „	16 30 „	2 0 W.
S. by W.	30 50 „	23 45 „	17 40 „	4 0 „
S.S.W.	29 30 „	23 50 „	18 15 „	5 10 „
S.W. by S.	27 30 „	23 50 „	18 40 „	6 0 „
S.W.	25 30 „	23 10 „	18 50 „	8 0 „
S.W. by W.	23 40 „	22 40 „	19 0 „	10 0 „
W.S.W.	21 30 „	21 45 „	18 40 „	11 50 „
W. by S.	19 0 „	20 30 „	18 0 „	13 30 „
West.	16 0 „	18 45 „	17 0 „	14 30 „
W. by N.	13 20 „	16 30 „	15 30 „	14 40 „
W.N.W.	10 0 „	13 40 „	13 10 „	14 0 „
N.W. by W.	6 40 „	10 50 „	10 20 „	12 30 „
N.W.	3 0 „	8 0 „	7 0 „	10 30 „
N.W. by N.	1 10 E.	4 35 „	3 40 „	7 45 „
N.N.W	5 40 „	0 20 „	0 0 „	5 0 „
N. by W.	10 30 „	4 10 E.	3 30 E.	2 0 „

XXI. *On the Construction of a new Calorimeter for determining the Radiating Powers of Surfaces in Air; and its Application to the Surfaces of various Mineral Substances.* By W. Hopkins, *Esq., M.A., F.R.S.*

Received June 1,—Read June 21, 1860.

When my paper on the Conductivity of various Substances was presented to the Society, it was intimated to me on the part of the Council of the Society, that it might be advisable to determine *absolute* instead of *relative* conductivities, the latter being alone attempted in my previous experiments. It has been partly in consequence of this intimation, as well as from the desire to make my investigations the more complete, that I have given my attention to the construction of a calorimeter which might serve for this purpose. The present communication contains a description of this instrument, with the results which it has enabled me to obtain respecting the absolute quantities of heat which emanate from the surfaces of certain substances under given conditions.

1. When a body is placed in atmospheric air (or any gas), the quantity of heat which is lost from its surface in a given time, when its temperature is higher than that of the surrounding medium, will be greater than if it were placed in a vacuum, other conditions remaining unaltered. In the latter case the heat escapes by simple radiation; in the other case a portion of the heat also escapes in consequence of the contact of the air with the surface of the heated body. Dulong and Petit ascertained by a careful series of experiments, the laws according to which the mercury contained in the bulb of a thermometer cools, or those which govern the quantity of heat which escapes from the surface of the containing bulb, when placed in a vacuum, in air, or in several kinds of gases. These experiments were made with the glass bulb naked, and also when it was silvered, so that the laws of radiation which they established were strictly in reference only to surfaces of glass and those of silver. Certain laws were identical in both these cases, and hence it was concluded, though by a limited induction, that the same laws were applicable to all other surfaces. They did not, however, give the *absolute* quantity of heat which, under given circumstances, and in a given time, emanates from the surfaces of the glass or silver with which they experimented. The instrument which I have constructed gives very easily this absolute amount of heat, as I believe, with very approximate accuracy.

The apparatus devised by Dulong and Petit is easily described with reference to its essential parts, and independently of the particular artifices which were required to secure its practical working. A hollow globe of thin copper, about a foot in diameter,

was firmly fixed in a vessel containing water in which the globe could be entirely immersed. An orifice existed in the upper side of the globe, through which a thermometer could be inserted and arranged so that the centre of its spherical bulb might coincide with the centre of the globe, and the orifice be hermetically closed. In making the experiment, the mercury of the thermometer was heated to any proposed temperature, and then rapidly placed in its position in the globe, where the rate of its cooling was determined by observing at regular intervals of time the temperature indicated by the graduated stem of the thermometer. The interior surface of the copper globe was blackened to prevent as much as possible all reflexion of heat, and was kept at a constant temperature by means of the water in which the globe was immersed. The experiments could thus be made at any temperature of the medium immediately surrounding the bulb, and also at any pressure of that medium, by withdrawing a portion of the atmospheric air, if that were the medium; or by withdrawing it entirely, and then filling the globe with any proposed gas at any assigned pressure. The rate at which the temperature of the mercury decreased gave a measure of the rate of its cooling, and consequently of the quantity of heat which emanated from the surface of the bulb in a given time under given conditions.

This apparatus was admirably adapted for experimenting with those substances of which the bulb of a thermometer might be formed, or with which the surface of the bulb could be uniformly and thinly coated; but was manifestly not applicable to determine the radiating power of the surfaces of mineral and many other substances. The simpler instrument which I have employed is equally applicable to all such surfaces, while it allows the extent of the radiating surface to be ascertained with greater accuracy than that of the bulb of the thermometer from which the radiation took place in the apparatus just described, and is so far better adapted for finding the absolute quantity of heat which radiates from a given area of a given surface in a unit of time. It does not, however, afford the means of determining the quantity of heat which radiates from a proposed surface in a vacuum, or when surrounded by different gases at various temperatures and pressures. To determine the laws of cooling in such cases, it was necessary to have recourse to some more complicated apparatus like that made use of by Dulong and Petit.

2. The laws of cooling of a body surrounded by air or gas, or when placed in a vacuum, as established by these able experimenters, are embodied in the following formula,—

$$Q = Aa^{\theta}(a^{t}-1)+Bp^{c}t^{b}, \quad \ldots \quad (1.)$$

where

Q=quantity of heat which escapes from the radiating surface in a given time;

a=1·0077, a numerical quantity which is the same for all radiating surfaces, and surrounding media;

θ=the uniform temperature of the surrounding vacuum or medium, expressed in Centigrade degrees;

t=excess of temperature of the radiating surface above that of the surrounding medium, in Centigrade degrees;

p=the pressure of the surrounding medium, expressed by the height of the mercurial column in metres, which the pressure of the medium supported;

c=a numerical value constant for the same surrounding medium at different temperatures, but different for different media; in the case of atmospheric air it =·45;

b=1·233, a numerical value which is the same for all radiating surfaces, surrounding media, and temperatures;

A and B are constants depending on the area of the radiating surface, and the time to which Q is referred.

When the radiation took place into a vacuum, the pressure p, and therefore the second term of the above formula vanished, and the quantity of heat which radiated in a given time was expressed by the first term, which exhibits the dependence of Q on θ, the temperature of the surrounding space (or of the physical surface which bounds that space), as well as on t, the excess of temperature of the radiating surface. This term will manifestly vary approximately as the simple power of t when the variations of t and θ are not too large. The second term expresses the quantity of heat carried off from the surface by the contact of a surrounding elastic medium, and expresses the law that this quantity is independent of the nature of the radiating surface, and depends on the surrounding medium only so far as regards the elasticity (p) of that medium, and not directly on its temperature, but only so far as the elastic force is affected by that temperature.

These conclusions, as applicable to all radiating surfaces, were made to rest, as I have already observed, on the somewhat narrow basis of induction from experiments on two kinds of surface only, those of glass and silver. Moreover the complete numerical values of A and B depend upon that of the area of the radiating surface, which, as remarked by MM. Dulong and Petit, was not easy to determine for the bulbs of their thermometers; nor, in fact, was it their object to determine the numerical value of the quantity of heat denoted by Q, but to ascertain the *laws* according to which the cooling of bodies takes place as depending on simple radiation into a vacuum, or on the contact of a circumambient medium.

It should also be remarked that these experiments can only be regarded as establishing the above formula for those cases in which the surrounding elastic medium is placed under the same conditions as in the apparatus with which the experiments were made. In another instrument these conditions might be different (as they are in that which I am about to describe), and the quantity of heat carried from the heated surface by convection might be different, while that due to radiation in vacuum must be the same. In other words, the relation between A and B might be different for different instruments. In adopting this formula I have assumed this relation to be the same for different instruments. The accordance which will be found between the quantity of heat calculated from the formula and that obtained by experiment, proves that the formula

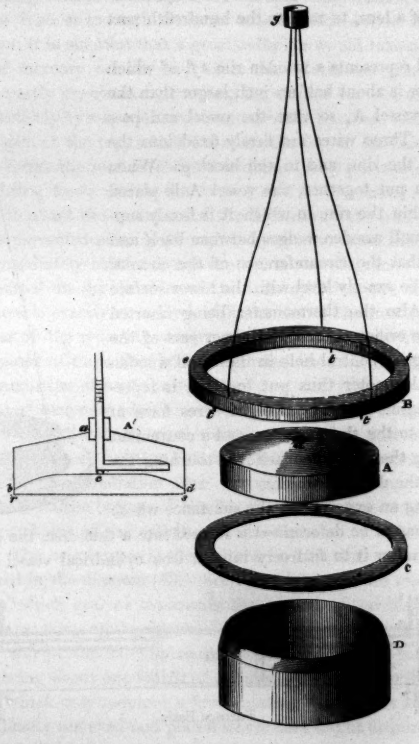
does give with approximate accuracy the whole quantity of heat which emanates from a given surface under the conditions imposed by the instrument, for any values of t between limits which may be inferred from the experiments themselves. This is sufficient for my principal object—that of determining the *absolute* conductivities of substances of which, in a former memoir, I have given only the *relative* conductivities. It is certain that the whole quantity of emanating heat given by the empirical formula is approximately correct; the relative values of the two terms may possibly not be equally so. All that is proved respecting their relation appears to be, that it is independent of the difference of temperatures denoted by t. I pretend not to enter on the problem of determining the quantities of heat carried off by a surrounding gas by convection and conduction respectively, under any assigned conditions.

Having the formula (1), we have next to determine the numerical values of the coefficients A and B. For this purpose, if effected independently, we should require two determinations of Q, for known values of θ, t, and p. In different series of experiments with radiating surfaces of the same nature (as glass, for example), the values of A are proportional to the areas of the radiating surfaces employed, the time during which the radiation takes place being always the same. These values also vary for surfaces of different kinds according to their radiating powers in a vacuum, of which it affords a relative measure. The values of B are considered the same for all surfaces, but are proportional to the areas of the radiating surfaces. Thus when an apparatus is used for the determination of Q, in which the area of the radiating surface is the same, one determination alone of B is required for any number of surfaces; and for the determination of A one experiment at least is necessary with each kind of surface. DULONG and PETIT determined these coefficients with great care for the surfaces of glass and silver, and the radiating surfaces (the bulbs of their thermometers) which they made use of; and for either of those kinds of surface the values of A and B, in any other sets of experiments with glass or silver, will only vary from the above in the ratio of the areas of the radiating surfaces. In the following comparisons of the results of calculation and observation, I have adopted the values of A and B determined by the French experimenters increased in the proper ratio. Thus, taking A_1 and B_1 to denote their coefficients for glass, we have

$$A = mA_1,$$
$$B = mB_1,$$
$$Q = m.A_1 a^{\theta}(a^{t}-1)+mB_1 p^{r}t^{s}, \quad \ldots\ldots\ldots\ldots \quad (2.)$$

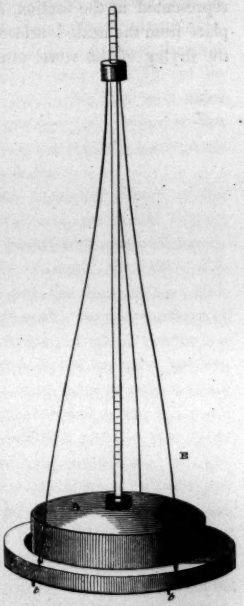
and one experiment only with glass is required theoretically for the determination of m. Also the coefficient mB_1, when once determined, is determined for all surfaces of equal extent; the coefficient mA_1 requires a separate determination for each kind of radiating surface. Practically the process has been to determine the mean value of m from a number of experiments, and then, adopting the corresponding values of the coefficients in (2.), to compare the calculated with the observed values. But before I enter into further details, I will describe the calorimeter which I have made use of.

3. In the accompanying diagrams A is a cylindrical tin vessel, of which A′ represents a vertical section through its axis. Its top is slightly conical, and has an orifice at its centre to admit the insertion of a thermometer; and its bottom is slightly curved as represented in the section, leaving a space *b c d s r* through which the radiation takes place from the heated surface in the position *r s*. The conical form of the top facilitates the drying of the vessel after it has been immersed in water to obtain a particular



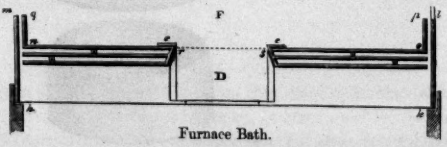
uniform temperature. The section also represents the thermometer used to ascertain the temperature of the distilled water with which the vessel is filled when the experiments are made with it. It is of the form of the letter L, the horizontal part being the bulb. The stem passes through a hole in the cork (*a*) which fits the central orifice, and

a small piece of cork is fastened on the heel of the instrument at *c*, on which the thermometer can be freely turned by the finger and thumb applied to the upper extremity of the stem. The horizontal bulb then becomes a most effective *stirrer* during the experiments, by maintaining it in constant rotation about the centre *c*. The thermometer is extremely delicate, each graduation of about $\frac{1}{10}$th of an inch corresponding to $\frac{1}{10}$th of a degree of FAHRENHEIT. It was easy, therefore, by the aid of a lens, to read to the hundredth part of a degree.



The diagram B represents a wooden rim *e f*, of which the inner diameter is about half an inch larger than the diameter of the vessel A, so that the vessel can pass freely within it. Three wires are firmly fixed into the upper surface of the rim, and to the block *g*. When the instrument is put together, the vessel A is placed concentrically within the rim, in which it is firmly supported by three small wooden wedges between itself and the rim, and so that the circumference of the circular bottom of A may be exactly level with the lower surface of the rim *e f*. Also the thermometer being inserted through *a* and the orifice corked, the upper part of the stem passes through a central hole in the small wooden block *g*. The calorimeter thus put together is represented by the diagram E. The upright wires form at once a protection to the thermometer, and a convenient means of handling the instrument without touching the vessel containing the distilled water.

4. In performing an experiment, the substance whose radiating power has to be determined is formed into a thin disc, the diameter of which is such as just to allow it to fit freely into an iron cylindrical vessel represented by D



Furnace Bath.

which contains such a quantity of mercury that the disc floating upon it shall have its upper surface exactly on a level with the rim of the cylinder. The required temperature is then given to the disc by heating the mercury on which it rests. This is effected, as represented in the diagram F, by placing the iron cylinder on the thin iron

plate $h\,k$ which forms the roof of the bath over the furnace, and is covered with a thin stratum of mercury, which is allowed to pass beneath the vessel and in contact with its bottom by means of three slightly projecting points on which the bottom rests. If a lower temperature than would thus be communicated directly to the mercury be required, it is easily regulated by the insertion of one or more iron discs beneath the iron cylinder, or if necessary, discs of paper or other bad conducting substances.

When the radiating surface is heated to the proper temperature, the calorimeter is to be placed above it so as to catch the heat which radiates from it. But if no precautions were taken, it is manifest that a great radiation would take place also from the heated stratum of mercury on $h\,k$, and affect the calorimeter placed over the iron cylinder. This is partly prevented by covering the surface $h\,k$ with cotton or other bad conductor, but effectively by a special contrivance for the purpose. $h\,k\,l\,m$ is the section of a square box, open at the top, which fits on to the top of the furnace, of which its sheet-iron bottom forms the roof as above described. $n\,o\,p\,q$ is the section of another square open box fitting freely within the former, and with a round hole in the centre just large enough to admit the insertion of the thin rim of the iron cylinder within it, which, however, is prevented passing through it by the increased thickness of the walls of the cylinder immediately below, as represented in the diagram. This inner box is thus entirely supported on the shoulder of the iron cylinder, and so that the internal surface of its bottom is exactly on a level with the rim of the iron cylinder, and therefore also, with that of the radiating surface of the disc placed within it. The bottom of the box is composed of three thin boards separated from each other, to prevent more effectively the transmission of heat through it.

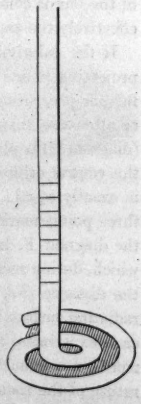
If the calorimeter were now placed over the radiating disc, it would rest with the projecting points t (figs. B and E) on the bottom of the box just described; but as a further precaution against all communication of heat to the calorimeter by conduction, or otherwise than by direct radiation from the radiating surface, a thin wooden rim (diagram C) is placed on the bottom of the box, but unattached to it, so as to surround the central orifice and rim of the cylinder, to the diameter of which its own diameter is exactly equal. The calorimeter is then placed on this rim, on which it rests at the three points marked in the diagram (C). Sections of this rim are represented by c, c in the diagram F, in which also $r\,s$ represents the section of the radiating surface, over which, during each experiment, the calorimeter is placed as represented in the diagram A′, the distance ($b\,r$, $d\,s$) of the circumference of the base of the calorimeter from the radiating surface being about one-fourth of an inch. On removing the calorimeter after each experiment (which only required a few minutes), the interior box $n\,o\,p\,q$, with the rim C, was immediately removed and placed where they might acquire again the temperature of the room before the next experiment.

It might have been supposed that it would be sufficient in the experiments, to place the circumference $b\,d$ (fig. A′) on the rim C, but in such case the results would have been entirely vitiated by the transmission of heat to the calorimeter by *conduction*, as I found

by tedious experience. In the above arrangement this risk is entirely obviated; for, it will be observed, there is no contact between the rim C and the supporting rim B except at three points; nor, again, is there any contact between the rim B and the vessel A, except at the three points at which they are connected by the wedges inserted between them.

The bottom of the tin vessel A was carefully coated with lamp-black, to prevent, as far as possible, the reflexion of the heat radiating upon it.

5. It has been already stated that the required heat is communicated to the mercury in the iron cylinder by placing it on the heated surface *h k* (fig. F). If the temperature required was less than 212° FAHR., the bath immediately beneath *h k* was filled with water, which was kept at the boiling temperature. When the iron cylinder rested immediately on the plate *h k*, the temperature of the mercury contained in it would rise to nearly 200°, and could be maintained at any lower temperature by placing a sufficient thickness of discs of iron, wood or other substances immediately beneath the cylinder. In this manner the *steadiness* of the temperature could be carefully preserved for any length of time, an essential condition in making the experiments. When the radiating surface was that of glass or iron, the discs of those substances could be rendered extremely thin, so that the temperature of the surface of radiation was very nearly equal to that of the mercury on which they floated, to which it might be considered as approximately equal, or to differ from it by a small correction. The temperature of the mercury immediately beneath the disc was ascertained by a thermometer, the small spherical bulb of which was inserted into it through a small hole in the centre of the disc for that purpose. In the cases of mineral substances (as limestone, sandstone, &c.), the discs could not be made thin enough to prevent a considerable difference of temperature between their upper radiating surfaces and their lower surfaces resting on the mercury. The temperature of the upper surface was then determined by a thermometer made for the purpose with a *spiral bulb* (as represented in the annexed diagram), the coils of the spire lying in one plane perpendicular to the graduated stem. A hollow was worked in the centre of the surface of the disc of sufficient diameter to receive the spiral bulb, and of such a depth that the bulb, when thus inserted, could be easily covered with mercury. The necessary depth did not exceed one-eighth of an inch, so that the temperature indicated by the thermometer, with its bulb placed in the hollow and covered with mercury, was necessarily very approximately that of the surface itself of the disc. Had a thermometer with an ordinary bulb been used, the central hollow must have been considerably deeper, and might therefore have been materially different from that of the outer surface, on account of the rapidity with which the temperature varies in a thin disc, in passing from its lower surface in contact with the mercury to the



outer one radiating into the atmosphere, when the temperature of the lower surface is much higher than that of the atmosphere*.

6. We may now proceed to describe the manner of conducting each experiment, the radiating surface having attained its required stationary temperature, and the calorimeter being filled with distilled water. A vessel containing water was placed near at hand, the temperature of the water being kept a little lower than that of the surrounding atmosphere of the room. The calorimeter was then immersed in this water, and allowed to remain there till the temperature of the distilled water and the tin vessel (A) containing it became stationary, as indicated by the sensitive L-shaped thermometer already described. It was then taken out of the water, and all the moisture adhering to it externally very carefully removed. The temperature would then remain sensibly stationary, and a little lower than that of the surrounding air. The thermometer was then carefully read, and the calorimeter transferred to its position above described, immediately over the radiating surface. After remaining there a certain observed time (during which the distilled water in it was thoroughly *stirred* as above described), it was removed, and the thermometer again read. The difference of the readings afforded a measure of the quantity of heat which had emanated from the heated surface and been absorbed by the vessel A of the calorimeter through its bottom, the observed result being subject to certain corrections to be hereafter considered.

The time during which the calorimeter was exposed to the influence of the radiating surface was determined with great accuracy. It seldom exceeded five or six minutes, generally not more than three or four. An assistant placed close to his ear a watch which *ticked* very audibly 150 times in a minute. It was easy to indicate to him the exact instant when the calorimeter was placed over the radiating surface, and he then began to count aloud the beats of the watch to a number varying according to the circumstances of each experiment, from 300 to 1000. The instrument was rapidly removed at the instant the counting of the number fixed upon was completed. The error to which the experiments were liable in this estimation of the *time* was very small.

I was also able to make the *readings* of the thermometer very accurately. I have stated that the first reading was made while the mercury was stationary. Such was the case also with the second reading; the rise of the thermometer of the calorimeter during an experiment seldom exceeded three or four degrees, and therefore the temperature of the distilled water and its containing vessel, when just removed from the influence of the radiating surface, differed from that of the surrounding atmosphere only by a small amount. Consequently the thermometer remained sensibly stationary for a longer time than was required to read it with care. I was thus able to obtain the reading with ease within the hundredth part of a degree of FAHRENHEIT.

* It might seem that a *flat* bulb would have answered the purpose, and been more simple in construction; but it was pointed out to me by Mr. CASELLA that thermometers of this construction are not to be relied upon. They may yield to a small external pressure sufficiently to affect the indication of temperature to the amount of several degrees.

Thus I could observe with great accuracy both the time during which radiation took place, and the increase of temperature acquired in that time by the calorimeter, and these are manifestly the two principal quantities to be determined by observation in the experiments. There are several possible sources of error, however, which require examination.

7. The first obvious consideration is that the water contained in the vessel A of the calorimeter does not, during the experiment, merely receive heat from the heated radiating surface; it will also, at each instant, be gaining or losing heat by the exposure of its external surface to the atmosphere, whenever its temperature differs from the surrounding temperature. I endeavoured to obviate this in the first place by making the vessel A of tin, the external surface of which, exposed to the atmosphere, was *polished*, while that exposed to the radiation from the heated disc, as already stated, was covered with lamp-black. The external surface was therefore a bad radiator of heat from within to the external air, and a bad absorbent of heat from without, and consequently helped to reduce the influence of the external air. Further, it is manifest that no effect could be produced on the experimental results, provided the *mean* temperature indicated by the thermometer of the calorimeter during an experiment were equal to the temperature of the external air. This condition was more or less approximately satisfied in the actual experiments, the results of which have been relied upon; but when not satisfied, it was easy to ascertain and apply the requisite correction when of sufficient amount to be sensible. To ascertain this correction, I made the following experiment. The whole instrument (E) was placed on an iron disc; it rested on its three feet (t). The vessel (A) of the calorimeter and the iron disc were immersed in water, of which the temperature was about 5° below that of the surrounding air. When the temperature indicated by the sensitive thermometer of the calorimeter had become perfectly stationary, the instrument and iron disc were taken out of the water, rapidly cleared of the external moisture, and the instrument replaced on the iron disc in the air. The under blackened surface of the vessel A was now exposed only to the surface of the iron disc, which was of the same temperature as the distilled water in A, and could not, therefore, affect its temperature. At the same time the external polished surface of A was exposed to the external air, of which the temperature was about 5° higher than that of the water of the calorimeter. The result, however, was that the thermometer of the calorimeter remained sensibly quite stationary for a considerably longer time than that required for any of the experiments, thus proving that the corrections in my actual experiments due to this cause were of insensible amount.

8. When a thin metal disc was used for the radiating surface, a small orifice was made at its centre, as above stated, just large enough to admit the bulb of a thermometer used to determine the temperature of the mercury beneath the disc. Over the area of this orifice the radiation took place from the surface of mercury, and not from that of the disc. Also, when a thicker disc of a mineral substance was used, the superficial hollow for the coiled bulb of the thermometer was filled with mercury, from the surface of

which, therefore, in the area occupied by it, the radiation took place instead of the radiation from the surface of the disc itself. It will be necessary to examine whether our experimental results were sensibly affected by the difference of radiation in these cases from the mercury and that from an equal extent of the discs made use of. Thus let

r=radius of the radiating disc;

ρ=radius of the central portion where the radiation takes place from mercury;

T=temperature of the radiating surface;

R=reading of the thermometer of the calorimeter, *i. e.* the temperature of its lower surface, on which the radiating heat falls;

then will

$$c(\mathrm{T}-\mathrm{R}) \quad \text{and} \quad \varpi(\mathrm{T}-\mathrm{R})$$

express the quantities of heat which emanate in air from a superficial unit of the respective surfaces of mercury and glass. The coefficients c and ϖ may be considered approximately as constant for variations of T−R which are not too large, but their ratio (which alone is required for the correction) is easily deduced from the experiments to be given in the sequel, for comparatively large values of T−R. Then if Q_1 be the observed quantity of heat which emanates from the disc in a given time,

$$\mathrm{Q}_1=\pi r^2\varpi(\mathrm{T}-\mathrm{R})-\pi\rho^2(\varpi-c)(\mathrm{T}-\mathrm{R})$$
$$=\pi r^2\varpi(\mathrm{T}-\mathrm{R})\left\{1-\frac{\rho^2}{r^2}\frac{\varpi-c}{\varpi}\right\},$$

or if Q=the quantity of heat which would emanate from the whole disc without the central orifice,

$$\mathrm{Q}_1=\mathrm{Q}\left\{1-\frac{\rho^2}{r^2}\left(1-\frac{c}{\varpi}\right)\right\},$$

$$\mathrm{Q}=\mathrm{Q}_1\left\{1+\frac{\rho^2}{r^2}\left(1-\frac{c}{\varpi}\right)\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

very nearly. The second term, $\frac{\rho^2}{r^2}\left(1-\frac{c}{\varpi}\right)\mathrm{Q}_1$, is the correction required. In my experiments this quantity is always small, but in some of them it is sensible.

9. Again, when discs of glass and metal were used, it was the temperature of the mercury on which they rested that was observed, *i. e.* the temperature of the *lower* surface of the disc. It becomes necessary, therefore, to examine what correction ought to be applied to this observed temperature, in order to obtain that of the upper or radiating surface. Now if t_1 be the temperature of the lower surface of the plate, t_2 that of its upper surface, τ that of surrounding space, or of a surface (like the lower one of the calorimeter) on which the radiation takes place, h the thickness of the plate, k its conducting power, and ϖ the radiating power of its surface in air, we have the approximate formula used in my last memoir (where the symbol p was used instead of ϖ),

$$\frac{k}{\varpi}=\frac{t_2-\tau}{t_1-t_2}h.$$

Hence we obtain

$$t_2 = t_1 \frac{\left(1+\frac{h\varpi}{k}\frac{\tau}{t_1}\right)}{1+\frac{h\varpi}{k}};$$

or since, in the present case, h is very small, we have approximately

$$t_2 = t_1\left\{1-\left(1-\frac{\tau}{t_1}\right)\frac{h\varpi}{k}\right\},$$

the real temperature of the radiating surface. Hence if Q_1 denote the observed quantity of heat which radiates from the disc, and Q the quantity which would radiate if the temperature of the disc's upper surface were t_1, we have

$$Q_1 = Q\left\{1-\left(1-\frac{\tau}{t_1}\right)\frac{h\varpi}{k}\right\};$$

and therefore

$$Q = Q_1\left\{1+\left(1-\frac{\tau}{t_1}\right)\frac{h\varpi}{k}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

very nearly. The second term, $Q_1\left(1-\frac{\tau}{t_1}\right)\frac{h\varpi}{k}$, is the correction required.

In my former experiments on conductivity, $\frac{k}{c}$ was the quantity determined, c being the radiating power of mercury in air, the upper surface of the substance experimented on having been always covered with mercury, from which, consequently, the radiation took place. The above correction may be put in the form (somewhat more convenient for application) of

$$Q_1\left(1-\frac{\tau}{t_1}\right)\frac{hc}{k}\cdot\frac{\varpi}{c}.$$

It is always a very small quantity.

10. Another correction requires to be carefully examined. In order that the calorimeter should receive directly on its blackened lower surface the whole of the heat emanating from the heated radiating surface, it would be necessary that the circumference or rim of its lower surface should coincide with the circumference of the radiating disc. But this condition cannot be accurately satisfied without the risk, as already explained, of deranging the experiments by heat passing to the calorimeter by *conduction*. It was to avoid this the more effectively that the wooden annulus (fig. C) was introduced, and thus a small interval of about the thickness of the wooden annulus existed between the circumference of the hollow bottom of the calorimeter and that of the radiating disc. This interval was equal to 0·21 inch. The heat which radiated on this intervening annulus would not immediately affect the calorimeter, and ought therefore to be added to the quantity which radiated directly on the calorimeter, and was measured by the indications of its thermometer.

The quantity of heat which radiates directly from the heated disc and fell on any

assigned portion of the bottom of the calorimeter (or the corresponding portion of the hemispherical surface of which the radiating surface was a diametral plane) is not easily determinable, on account of the complicated integration to which the investigation leads. It is easy, however, to compare very approximately the amount which thus falls on a very narrow annulus of the hemispherical surface contiguous to the diametral plane formed by the radiating surface, with the whole quantity which radiates from that surface in a given time. Thus let

δq = the quantity of heat which radiates in a unit of time from the small element δS of the radiating surface, and falls on the indefinitely small area w of the above-mentioned hemisphere;

I = the intensity of normal radiation;

E = angle of emanation, and therefore $I.\sin E$ = the intensity of radiation in a direction making an angle E with the radiating surface;

φ = angle of incidence on ω;

r = distance of ω from δS;

ρ = projection of r on the radiating diametral surface;

θ = angle which ρ makes with the diameter of the diametral plane passing through the projection of ω on that plane;

q' = the quantity of heat which radiates on the element ω;

then

$$\delta q' = I.\frac{\omega \cos \varphi}{r^2} \sin E.\delta S;$$

and if z_1 denote the distance of w from the diametral plane,

$$\sin E = \frac{z_1}{r};$$

Also

$$\delta S = \rho \delta\theta \delta\rho.$$

The angle φ is that which r makes with the normal to the surface at ω. Instead of expressing its general value, suppose ω to be situated within the diametral annulus above mentioned, and therefore very near to the diametral plane; it may then be considered as lying on the axis of z, assuming the origin of coordinates to be at the extremity of the diameter from which θ is measured. The normal to the point ω may then also be considered as parallel to that diameter, the axis of x, and we shall have

$$\cos \varphi = \frac{x}{r},$$

$$= \frac{\rho \cos \theta}{r}.$$

Hence

$$\delta q' = I\omega z_1 \frac{\rho^2}{r^4} \cos \theta \delta\theta \delta\rho,$$

$$= I\omega z_1 \frac{\rho^2}{(z_1^2 + \rho^2)^2} \cos \theta \delta\theta \delta\rho;$$

and

$$q' = \mathrm{I}\omega z_1 \int \frac{\varrho^2 d\varrho}{(z_1^2+\varrho^2)^{\frac{3}{2}}} (\sin\theta + \mathrm{C}).$$

The proper limits of θ are $\pm \cos^{-1}\frac{\varrho}{2a}$ (a= radius of the diametral surface), but they would render the next integration unmanageable. Take the integral from $\theta = -\frac{\pi}{2}$ to $\theta = \frac{\pi}{2}$. Then

$$q' = 2\mathrm{I}\omega z_1 \int \frac{\varrho^2 d\rho}{(z_1^2+\varrho^2)^{\frac{3}{2}}}$$

$$= 2\mathrm{I}\omega z_1 \left\{ \mathrm{C} - \frac{\varrho}{2(z_1^2+\varrho^2)} + \frac{1}{2z_1} \tan^{-1}\frac{\varrho}{z_1} \right\}$$

$$= \mathrm{I}\omega \left\{ \tan^{-1}\frac{\varrho}{z_1} - \frac{\varrho z_1}{z_1^2+\varrho^2} \right\}$$

since q' vanishes with ϱ.

With the increase of ϱ (z_1 being very small) this expression rapidly approximates to

$$\mathrm{I}\omega\frac{\pi}{2};$$

i. e. if z_1 be sufficiently small we shall have approximately

$$q' = \frac{\pi}{2}\mathrm{I}.\omega;$$

or since the ω is an element of our narrow diametral annulus, we have

$$q = \frac{\pi}{2}\mathrm{I}.\text{ area of the annulus},$$

q being the quantity of heat which radiates upon the annulus. If the breadth of the annulus be denoted by β, its area will $= 2\pi a\beta$, and

$$q = \pi^2 \mathrm{I} a\beta.$$

Again, let Q be the quantity of heat which radiates in a unit of time from the whole radiating surface. Conceive two right cones with common vertex at δS and common axes perpendicular to the radiating surface, their vertical angles being θ and $\theta+\delta\theta$. The quantity of heat radiating between these two conical surfaces will

$$= \delta\mathrm{S}.\mathrm{I}\cos\theta.2\pi\sin\theta.\delta\theta,$$

and therefore the whole quantity radiating from δS will

$$= \delta\mathrm{S}.\pi\mathrm{I}\int_0^{\frac{\pi}{2}} \sin 2\theta d\theta,$$

$$= \delta\mathrm{S}.\pi\mathrm{I},$$

or $$\delta\mathrm{Q} = \pi\mathrm{I}.\delta\mathrm{S},$$

$$\therefore \quad \mathrm{Q} = \pi\mathrm{I}.\pi a^2$$

$$= \pi^2 \mathrm{I} a^2.$$

Hence

$$\frac{q}{Q}=\frac{\beta}{a}$$

$$=\frac{\text{breadth of the annulus}}{\text{rad. of radiating surf.}}.$$

Hence taking Q_1 as before,

$$Q=Q_1\left\{1+\frac{\beta}{a}\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.)$$

The expression above obtained for q will only be accurately true when β is indefinitely small, as is easily seen from the limits which have been taken for θ and ϱ in the integration. If β be small but finite, as in our actual case, the above value of q will be approximately true, but somewhat too large.

It may be doubted whether the above investigation is strictly applicable to the whole of the heat which emanates from the heated surface or to that part only which may be conceived to *radiate* through the air to the bottom of the calorimeter, in contradistinction to that which must be borne away by the air from the heated surface by *convection* or *conduction*. As the effect, however, produced on the narrow annulus must be of the same kind, there is probably little error in the correction, by supposing it of the same magnitude.

11. There is another error, which would seem perhaps to be inherent in any experimental determination of the quantity of heat radiating from one surface and falling on another. It arises from the fact of one of these surfaces (as the base of the calorimeter in my experiments, and the internal surface of the surrounding globe in those of Dulong and Petit) not being *perfectly absorbent*, as assumed in the results, which ought, therefore, in the following experiments, to be increased in the proportion which the heat reflected from the blackened surface of the calorimeter bears to the heat absorbed by it. This ratio is probably very small, but I am not aware of any attempt to determine it.

Numerous experiments were made before the calorimeter assumed exactly the form above described; for it was only by a careful observation of the anomalies presented by the earlier experiments that I became fully aware of the importance which attached to different points in the construction of the instrument, and the mode of conducting the experiments. I shall give a few of the later experiments, on which some of my principal results are founded, in full detail, to enable the reader the better to judge of the confidence to which they may be entitled. The following experiments on a glass disc were made for the determination of m (art. 3).

12. Let T_1 = temperature of the radiating surface when the experiment begins;

T_2 = ditto when it ends;

R_1 = reading of the thermometer of the calorimeter at the beginning of the experiment;

R_2 = ditto at the end of it;

then will $\frac{1}{2}(T_1+T_2)$ be the mean temperature of the radiating surface during the experiment, and R_2-R_1 will = the rise in the temperature of the calorimeter during the observed time of the experiment, expressed in the number of beats of the watch. The time was usually taken longer or shorter, according as the rise of the thermometer of the calorimeter was slower or faster. Five hundred beats corresponded to 3·333 minutes.

It will be observed that in each of the experiments (1), (2), &c. in each series I., II., &c., the temperatures of the radiating surface are approximately equal. These experiments, (1), (2), &c., are in fact repetitions of nearly the same experiment, made with the view of obtaining the mean result of several experiments instead of relying on the result of one. And here I may remark that this was necessary, not merely for the elimination of errors of observation, but also for that of the actual irregularities in the rising of the mercury in the thermometer of the calorimeter. Moreover no high temperature can be maintained perfectly stationary, but is always in a state of oscillation about a mean value. If every experiment could be made *exact*, the numbers registered in the fourth column of the following Table ought to be the same. The irregularities which they present are partly due to the slightly different temperatures (as exhibited in the second and third columns) at which the experiments were made, partly to the causes just mentioned, and partly to the necessary errors of observation. All these irregularities may manifestly be more or less eliminated by taking the mean result derived from a number of similar experiments. For this purpose I have taken the mean (T) of the tabulated values of T_1 and T_2, and the mean (R) of the values of R_1 and R_2, and considered (T)−(R) as the difference between the temperature of the radiating surface and that of the lower blackened surface of the calorimeter to which the heat emanating from the radiating surface was immediately communicated; while the mean of the numbers in the fourth column is taken as the corresponding rise in the temperature of the calorimeter. An inspection of these columns will show how far the result of each individual experiment differs from the mean result, and will afford a measure of the reliance which may be placed on this mode of experimenting.

I. Disc of *Glass*.

Time, or duration of each experiment =500 beats.
Height of barometer . . . . . =30·5 inches.
= ·77 metre.

Number of the experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $= R_2 - R_1$.	Temperature of the air.
			°	°
(1)	$T_1 = 150{\cdot}0$	$R_1 = 60{\cdot}72$ $R_2 = 62{\cdot}24$	1·52	64
(2)	$T_1 = 151{\cdot}2$ $T_2 = 159{\cdot}8$	$R_1 = 61{\cdot}39$ $R_2 = 63{\cdot}00$	1·61	
(3)	$T_1 = 150{\cdot}0$ $T_2 = 149{\cdot}5$	$R_1 = 59{\cdot}91$ $R_2 = 61{\cdot}50$	1·59	
(4)	$T_1 = 149{\cdot}2$ $T_2 = 147{\cdot}0$	$R_1 = 61{\cdot}25$ $R_2 = 62{\cdot}77$	1·52	
(5)	$T_1 = 147{\cdot}0$ $T_2 = 147{\cdot}5$	$R_1 = 61{\cdot}70$ $R_2 = 63{\cdot}16$	1·56	
(6)	$T_1 = 147{\cdot}5$ $T_2 = 147{\cdot}5$	$R_1 = 62{\cdot}00$ $R_2 = 63{\cdot}45$	1·45	64
(7)	$T_1 = 147{\cdot}7$ $T_2 = 147{\cdot}7$	$R_1 = 61{\cdot}84$ $R_2 = 63{\cdot}27$	1·43	
(8)	$T_1 = 148{\cdot}6$ $T_2 = 148{\cdot}8$	$R_1 = 61{\cdot}95$ $R_2 = 63{\cdot}46$	1·51	
(9)	$T_1 = 149{\cdot}6$ $T_2 = 149{\cdot}6$	$R_1 = 62{\cdot}89$ $R_2 = 64{\cdot}40$	1·51	

Hence we obtain the following mean values:—

$$(T) = 148°{\cdot}20 \text{ (F.)},$$
$$(R) = 62°{\cdot}27;$$
$$\therefore \quad (T) - (R) = 85°{\cdot}93.$$

When (R) is expressed in *Centigrade degrees*, its numerical value becomes that of θ in our general formula; and the value of (T)—(R) in the same degrees, is that of t in the formula. Hence for the mean of the above nine experiments,

$$\theta = 16°{\cdot}80,$$
$$t = 47°{\cdot}74.$$

Also, taking the mean of the tabulated values,

$$R_2 - R_1 = 1{\cdot}52.$$

II. Same Disc of *Glass*.

Time . . . . . = 300 beats.
Height of barometer = 30·25 inches.
= ·76 metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $= R_2 - R_1$.	Temperature of the air.
(1)	$\left\{\begin{matrix} T_1 = 246°0 \\ T_2 = 244°5 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·55 \\ R_2 = 64·98 \end{matrix}\right\}$	2·43°	
(2)	$\left\{\begin{matrix} T_1 = 246·5 \\ T_2 = 245·0 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·61 \\ R_2 = 65·00 \end{matrix}\right\}$	2·39	63°
(3)	$\left\{\begin{matrix} T_1 = 247·1 \\ T_2 = 246·6 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·65 \\ R_2 = 65·23 \end{matrix}\right\}$	2·58	64
(4)	$\left\{\begin{matrix} T_1 = 248·4 \\ T_2 = 247·4 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·64 \\ R_2 = 65·26 \end{matrix}\right\}$	2·62	
(5)	$\left\{\begin{matrix} T_1 = 248·8 \\ T_2 = 248·5 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·61 \\ R_2 = 65·14 \end{matrix}\right\}$	2·53	64·5
(6)	$\left\{\begin{matrix} T_1 = 249·2 \\ T_2 = 248·0 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·59 \\ R_2 = 65·05 \end{matrix}\right\}$	2·46	
(7)	$\left\{\begin{matrix} T_1 = 249·3 \\ T_2 = 249·0 \end{matrix}\right\}$	$\left\{\begin{matrix} R_1 = 62·65 \\ R_2 = 65·10 \end{matrix}\right\}$	2·45	
(8)	$T_1 = 249·5$	$\left\{\begin{matrix} R_1 = 62·50 \\ R_2 = 64·97 \end{matrix}\right\}$	2·47	64

Hence we obtain

$$(T) = 247°·6 \text{ (F.)},$$
$$(R) = 63°·81,$$
$$(T) - (R) = 183°·79;$$

and hence, for the mean of these eight experiments,

$$\theta = 17°·6 \text{ (C.)},$$
$$t = 102°·1;$$

and the mean value of

$$R_2 - R_1 = 2·49.$$

This is for the time of 300 beats; therefore for 500 beats we have, as a mean value,

$$R_2 - R_1 = 4·16.$$

III. Same Disc of *Glass*.

Time . . . . . =300 beats.
Height of barometer =30·3 inches.
= ·76 metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$\left\{\begin{matrix}T_1=378°·5\\T_2=378·5\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=60·81\\R_2=66·25\end{matrix}\right\}$	5°·44	62°
(2)	$\left\{\begin{matrix}T_1=380·0\\T_2=380·5\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=61·02\\R_2=66·20\end{matrix}\right\}$	5·18	
(3)	$\left\{\begin{matrix}T_1=381·5\\T_2=380·0\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=58·53\\R_2=63·74\end{matrix}\right\}$	5·21	61
(4)	$\left\{\begin{matrix}T_1=380·0\\T_2=381·3\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=58·90\\R_2=64·10\end{matrix}\right\}$	5·20	
(5)	$\left\{\begin{matrix}T_1=384·0\\T_2=382·5\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=59·13\\R_2=64·55\end{matrix}\right\}$	5·42	62
(6)	$T_1=378·0$	$\left\{\begin{matrix}R_1=59·36\\R_2=64·74\end{matrix}\right\}$	5·38	
(7)	$\left\{\begin{matrix}T_1=375·5\\T_2=376·0\end{matrix}\right\}$	$\left\{\begin{matrix}R_1=59·63\\R_2=65·10\end{matrix}\right\}$	5·47	

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Taking the means, we obtain

$$(T)=379°·70 \text{ (F.)}$$
$$(R)=\ 62°·29,$$
$$(T)-(R)=317°·41;$$

and hence from the mean of these seven experiments we have

$$t=\ 16°·6 \text{ (C.)},$$
$$t=175°·4,$$
$$R_2-R_1=\ 5·33 \text{ for 300 beats},$$

and therefore

$$R_2-R_1=\ 8·88 \text{ for 500 beats}.$$

13. Recurring to equation (2.), art. 3, and substituting the numerical values for A_1 and B_1, adopted by DULONG and PETIT, we have

$$Q=m\{2·037a^t(a^t-1)+·00919p^{·45}t^{1·233}\};$$

or putting the last term in a form which may in some cases be rather more convenient for numerical calculation, we shall have

$$Q=m\{2·037a^t(a^t-1)+·00793\left(\frac{p}{·72}\right)^{·45}t^{1·233}\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.)$$

Our first object is the determination of m, and for this purpose we must substitute

successively in this equation, the values of θ, t, and p above given as mean values in the series of experiments I., II., and III., and for Q we substitute the corresponding mean values of $R_2 - R_1$, the increase of temperature of the calorimeter due to the radiation upon its lower surface. The quantity of heat represented by Q will thus be measured numerically by the number of FAHRENHEIT degrees by which the temperature of the water in the instrument is augmented. This numerical value may be represented by Q°. Its proper numerical value will be introduced hereafter.

After tedious numerical calculation, in which I feel satisfied there is no material error, the following values of m were derived from the three series respectively.

$$\text{I. } t = 47^\circ{\cdot}7 \text{ (C.)}, \quad m_1 = \frac{1{\cdot}52}{1{\cdot}98} = {\cdot}77;$$

$$\text{II. } t = 101^\circ{\cdot}6 \text{ (C.)}, \quad m_2 = \frac{4{\cdot}16}{5{\cdot}18} = {\cdot}80;$$

$$\text{III. } t = 175^\circ{\cdot}4 \text{ (C.)}, \quad m_3 = \frac{8{\cdot}88}{11{\cdot}33} = {\cdot}78;$$

$$\text{Mean value of } m = m_0 = {\cdot}783.$$

I have above stated the various corrections which ought to be applied to the values of $R_2 - R_1$, or of Q in the last formula. They will lead to a corrected value of m_0, which we may now proceed to find. These corrections are as follows:—

(1) *Correction due to the influence of the external air.*—It will be remarked that the difference between this temperature and θ, that of the calorimeter in the preceding experiments, is very small. The correction is inappreciable.

(2) *The correction due to the central orifice in the glass disc* (art. 8).—In the formula of that article

$$\frac{\varrho^2}{r^2} = {\cdot}006.$$

The ratio $\frac{c}{\varpi}$ is found from the experiments which determine the whole radiation in air from the surfaces of mercury and glass to be somewhat different for different temperatures. It may be taken as follows in the mean of each of the preceding series:—

$$\text{In I. } \frac{c}{\varpi} = {\cdot}6 \text{ nearly,}$$

$$\text{In II. } \frac{c}{\varpi} = {\cdot}7 \text{ nearly,}$$

$$\text{In III. } \frac{c}{\varpi} = {\cdot}8 \text{ nearly.}$$

Hence the formula (3.) of art. 8 becomes

$$\text{In I. } Q^\circ = Q_1 \{1 + {\cdot}0064(1 - {\cdot}6)\}$$
$$= 1{\cdot}52\{1 + {\cdot}0025\},$$
$$\text{In II. } Q^\circ = 4{\cdot}16\{1 + {\cdot}0019\},$$
$$\text{In III. } Q^\circ = 8{\cdot}88\{1 + {\cdot}0013\}.$$

(3) *Correction due to the thickness of the disc.*—This correction must be applied, like the last, to the mean values of Q derived from each of the series of experiments I., II., and III. Now in

$$\text{I.}\quad \begin{cases} t_1 = 148^\circ \text{ (F.) nearly,} \\ \frac{c}{\varpi} = \cdot 6 \text{ (as in (2)).} \end{cases}$$

$$\text{II.}\quad \begin{cases} t_1 = 248^\circ \text{ (F.),} \\ \frac{c}{\varpi} = \cdot 7. \end{cases}$$

$$\text{III.}\quad \begin{cases} t_1 = 380^\circ \text{ (F.),} \\ \frac{c}{\varpi} = \cdot 8. \end{cases}$$

Also we may take as a mean value of τ for I., II. and III.,

$$\tau = 63^\circ \text{ nearly.}$$

The thickness of the glass plate we have

$$h = \tfrac{1}{16} \text{ inch,}$$
$$= \cdot 005 \text{ foot;}$$

and for glass, I assume

$$\frac{k}{c} = 1 \cdot 0^*;$$

and therefore for our glass plate the values of $\frac{hc}{k} \cdot \frac{\varpi}{c}$ are

$$\cdot 008 \text{ in experiment I.}$$
$$\cdot 007 \text{ in experiment II.}$$
$$\cdot 006 \text{ in experiment III.}$$

Also the values of $1 - \frac{\tau}{t_1}$ $\left(\text{or of } 1 - \frac{(R)}{(T)} \text{ in the experiments}\right)$ become

$$\cdot 6 \text{ in I.}$$
$$\cdot 75 \text{ in II.}$$
$$\cdot 83 \text{ in III.}$$

and the formula (4.), art. 9, becomes in

$$\text{I.}\quad Q^s = 1 \cdot 52\{1 + \cdot 0048\}.$$
$$\text{II.}\quad Q^s = 4 \cdot 16\{1 + \cdot 0052\}.$$
$$\text{III.}\quad Q^s = 8 \cdot 88\{1 + \cdot 0050\}.$$

(4) We have finally to take the correction investigated in art. 10. On account of it we must take

$$Q = Q_1\left\{1 + \frac{\beta}{a}\right\}.$$

* I have not determined the conducting power of glass directly by experiment. I have assumed it to be the same as for the most compact igneous rock, as given in my former memoir.

Hence, putting $\frac{\beta}{a}=\frac{\cdot 21}{5\cdot 5}=\cdot 038$, we have

I. $Q^s=1\cdot 52\{1+\cdot 038\}$.

II. $Q^s=4\cdot 16\{1+\cdot 038\}$.

III. $Q^s=8\cdot 88\{1+\cdot 038\}$.

14. Applying all these corrections, we have

$$Q^s=Q_1^s\left\{1+\frac{\varrho^2}{r^2}\left(1-\frac{c}{\varpi}\right)+\left(1-\frac{\tau}{l_1}\right)\frac{hc}{k}\cdot\frac{\varpi}{c}+\frac{\beta}{a}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7.)$$

$$=Q_1^s\{1+E\} \text{ suppose.}$$

Consequently the observed values of Q (or R_2-R_1), the mean results of the series I., II., III. respectively, must be increased in the ratio

$1+E_1 : 1$ in series I.,

$1+E_2 : 1$ in series II.,

$1+E_3 : 1$ in series III.,

when we substitute them in equation (6.) for the purpose of determining m_1, m_2, and m_3; or since an alteration in Q will produce a proportional change in m (as is evident from the equation), we must increase m_1, m_2, and m_3 in the above ratios respectively; *i. e.* for their mean value m_0, we shall have

$$m_0=\cdot 783\{1+\tfrac{1}{3}(E_1+E_2+E_3)\}.$$

Now taking the sum of the corrections indicated in the above expression for Q, in each of the three series separately, we have

$$E_1=\cdot 0453$$
$$E_2=\cdot 0451$$
$$E_3=\cdot 0443$$
$$\frac{E_1+E_2+E_3}{3}=\cdot 045;$$

and hence we have, finally,

$$m_0=\cdot 783\{1+\cdot 045\}$$
$$=\cdot 818.$$

Finally, substituting this value of m in the formula (6.) of article 13, we have

$$Q^s=1\cdot 666\, a^s(a^t-1)+\cdot 00648\left(\frac{p}{\cdot 72}\right)^{\cdot 45} t^{1\cdot 233} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8.)$$

We may now compare the observed quantities of heat radiating from a surface of glass, as ascertained by the above three series of experiments, with the calculated values given by this formula. In doing this, it must be recollected that the formula gives the *whole* quantity of heat which radiates from the given glass surface, whereas the *observed* quantity is that which falls on the calorimeter. The correction E_3 must therefore be omitted, and the above formula becomes

$$Q^s=1\cdot 610\, a^s(a^t-1)+\cdot 00626\left(\frac{p}{\cdot 72}\right)^{\cdot 45}\cdot t^{1\cdot 233}.$$

Series of experiments.	Values of θ (C.).	Values of t (C.).	Calculated values of Q.	Observed values of Q.	Differences.
I.	16°·6	47°·7	1·56	1·52	0·04
II.	17·6	102·1	4·09	4·16	−0·07
III.	16·6	175·4	8·95	8·88	0·07

The small amount of the differences registered in the last column are sufficient to indicate the very approximate accuracy of the formula for at least a considerable range of temperature, as indicated by the values of t in the third column.

15. I now proceed to detail three other series of experiments similar to the above, with a *disc of Chalk* made as dry as possible.

IV. Disc of *Dry Chalk*.

Duration of each experiment = 1000 beats.
Height of the barometer . . = 30·33 inches.
= ·77 metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $= R_2 - R_1$.	Temperature of the air.
(1)	T=135°·2	$\left\{\begin{matrix} R_1=57°·92 \\ R_2=60·57 \end{matrix}\right\}$	2°·65	60°·5
(2)	T=135·6	$\left\{\begin{matrix} R_1=58·95 \\ R_2=61·60 \end{matrix}\right\}$	2·65	
(3)	T=135·6	$\left\{\begin{matrix} R_1=59·52 \\ R_2=62·17 \end{matrix}\right\}$	2·65	61
(4)	T=135·5	$\left\{\begin{matrix} R_1=59·28 \\ R_2=61·99 \end{matrix}\right\}$	2·71	61
(5)	T=136·4	$\left\{\begin{matrix} R_1=59·25 \\ R_2=61·76 \end{matrix}\right\}$	2·51	61·5

Hence, adopting the same notation as above for the mean values, we have

$$(T)=135°·66\ (F.),$$
$$(R)=\ 60°·30\ (F.)=15°·7\ \ (C.)=\theta,$$
$$(T)-(R)=\ 75°·36\ \ \ \ =41°·66\ (C.)=t.$$

Also, taking the mean of the "Differences,"

$$R_2-R_1=2·66 \text{ for } 1000 \text{ beats},$$
$$=1·33 \text{ for } \ 500 \text{ beats}.$$

V. Same Disc of *Chalk*.

Duration of each experiment $=500$ beats.
Height of the barometer . $=30{\cdot}22$ inches.
$=$ ·767 metre.

Number of experiment.	Temperature of the radiating surface.	Readings of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$T=213^\circ{\cdot}0$	$R_1=58^\circ{\cdot}85$, $R_2=61{\cdot}76$	$2^\circ{\cdot}91$	60°
(2)	$T=212{\cdot}7$	$R_1=58{\cdot}44$, $R_2=61{\cdot}36$	$2{\cdot}92$	
(3)	$T=213{\cdot}5$	$R_1=58{\cdot}50$, $R_2=61{\cdot}34$	$2{\cdot}84$	$60{\cdot}5$
(4)	$T=214{\cdot}4$, $T=215{\cdot}5$	$R_1=58{\cdot}14$, $R_2=61{\cdot}22$	$3{\cdot}08$	
(5)	$T=216{\cdot}2$	$R_1=58{\cdot}43$, $R_2=61{\cdot}39$	$2{\cdot}96$	$61{\cdot}5$

Hence we have

$$(T)=214^\circ{\cdot}2\ (F.),$$
$$(R)=\ 59^\circ{\cdot}94=15^\circ{\cdot}55\ (C.)=\theta,$$
$$(T)-(R)=154^\circ{\cdot}26=85^\circ{\cdot}7\ \ (C.)=t.$$

Also, taking the mean value of the "Differences,"

$$R_2-R_1=2{\cdot}94.$$

VI. Same Disc of *Chalk*.

Duration of each experiment . $=400$ beats.
Height of the barometer . . $=30{\cdot}22$ inches.
$=$ ·767 metre.

Number of experiment.	Temperature of the radiating surface.	Reading of the calorimeter.	Difference of the readings $=R_2-R_1$.	Temperature of the air.
(1)	$T=295^\circ{\cdot}5$	$R_1=58^\circ{\cdot}41$, $R_2=62{\cdot}68$	$4^\circ{\cdot}27$	$60^\circ{\cdot}5$
(2)	$T=296{\cdot}0$	$R_1=58{\cdot}19$, $R_2=62{\cdot}25$	$4{\cdot}06$	
(3)	$T=289{\cdot}5$	$R_1=58{\cdot}21$, $R_2=62{\cdot}25$	$4{\cdot}04$	$60{\cdot}5$
(4)	$T=288{\cdot}5$	$R_1=58{\cdot}30$, $R_2=62{\cdot}28$	$3{\cdot}98$	$61{\cdot}5$
(5)	$T=289{\cdot}0$	$R_1=58{\cdot}53$, $R_2=62{\cdot}60$	$4{\cdot}07$	

Hence we have

$$(T)=290°{\cdot}5=$$
$$(R)=\ 60°{\cdot}35\ (F.)=\ 15°{\cdot}75\ (C.)=\theta,$$
$$(T)-(R)=230°{\cdot}15\ (F.)=127°{\cdot}85\ (C.)=t;$$

and for the mean value

$$R_2-R_1=4{\cdot}08 \text{ for } 400 \text{ beats},$$
$$=5{\cdot}10 \text{ for } 500 \text{ beats}.$$

16. We may now apply these results to obtain the expression for the quantity of heat emanating from our chalk disc. Since its area is the same as that of the glass disc, the second term of the expression (2) of article 3 will be the same for all substances, and therefore the same as that already determined for glass. Thus we have

$$Q=Aa^{\theta}(a^{t}-1)+{\cdot}00648\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9.)$$

Q here represents the whole quantity of heat which would radiate under the conditions of the experiment, from a disc of chalk of the given area; but the observed values of this quantity, as represented by R_2-R_1 in the previous experiments, is the measure of the heat only which falls on the calorimeter, and consequently requires the two following corrections:—

(1) The temperature of the surface of the disc was obtained from that of the mercury occupying a shallow central hollow of which the diameter was 1·5 inch, that of the whole disc being 5·5 inches. Throughout this small central circle the radiation took place from mercury instead of chalk, and consequently a correction must be made similar to the correction investigated in article 8. Here we have

$$\frac{\rho^2}{r^2}={\cdot}074;$$

and in the series of experiments

IV. $\frac{c}{\varpi}={\cdot}58$ nearly.

V. $\frac{c}{\varpi}={\cdot}62$.

VI. $\frac{c}{\varpi}={\cdot}70$.

Hence, so far as depends on this correction,

$$Q^{0}=(R_2-R_1)\left\{1+\frac{\rho^2}{r^2}\left(1-\frac{c}{\varpi}\right)\right\}$$
$$=1{\cdot}33\{1+{\cdot}031\} \text{ in series IV.}$$
$$=2{\cdot}94\{1+{\cdot}028\} \text{ in series V.}$$
$$=5{\cdot}10\{1+{\cdot}022\} \text{ in series VI.}$$

(2) All the heat which emanates from the surface of the disc does not fall on the bottom of the calorimeter, as explained in article 10. Consequently a correction also

is required, such as is investigated in that article. Its amount is the same in all the experiments. Hence, on account of this correction, we have

$$Q'=(R_2-R_1)\left\{1+\frac{\beta}{a}\right\} \text{ (art. 10),}$$

$$=1{\cdot}33\{1+{\cdot}038\} \text{ in series IV.}$$

$$=2{\cdot}94\{1+{\cdot}038\} \text{ in series V.}$$

$$=5{\cdot}10\{1+{\cdot}038\} \text{ in series VI.}$$

Taking the sum of these two corrections in each series respectively,

$$Q'=1{\cdot}33(1{\cdot}069)=1{\cdot}42 \text{ in series IV.}$$

$$Q'=2{\cdot}94(1{\cdot}066)=3{\cdot}13 \text{ in series V.}$$

$$Q'=5{\cdot}10(1{\cdot}060)=5{\cdot}41 \text{ in series VI.}$$

These are the corrected values which are to be substituted for Q in the formula (9.). After the requisite numerical calculation, we thus obtain the following three values of A:

$$A=1{\cdot}781 \text{ from series IV.}$$

$$A=1{\cdot}420 \text{ from series V.}$$

$$A=1{\cdot}444 \text{ from series VI.}$$

Mean value $=1{\cdot}548$.

It will be observed that the first of these values of A is considerably larger than the two others. It is that which corresponds to the smallest value of the difference of temperature denoted by t, or R_2-R_1, and small values of this quantity are unfavourable for the accurate determination of A, since, in such case, a small error in the experimental result will lead to a considerable error in the value of A. The above mean value, 1·548, is probably too large, and I should rather adopt 1·5 as a more probable value, thus giving greater weight to the two last determinations than to the first. The formula (9.) then becomes

$$Q=1{\cdot}500\,a^t(a^t-1)+{\cdot}00648\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}. \quad . \quad . \quad . \quad . \quad . \quad (10.)$$

Comparing the values of Q obtained from this formula, with the values of R_2-R_1 as corrected above, we have the following results:—

Comparison of the Observed and Calculated Values of Q for *Dry Chalk*.

Series of experiments.	Values of θ (C.).	Values of t (C.).	Calculated values of Q.	Corrected observed values of Q.	Differences.
IV.	15·7	41·66	1·29	1·42	·13
V.	15·55	85·70	3·19	3·13	·06
VI.	15·75	127·85	5·46	5·41	·05

17. Three similar series of experiments were made with a disc of *New Red Sandstone*. It will be sufficient, I conceive, to give the results without details, which are exactly

similar to those given in the preceding series. Calling these series VII., VIII., IX., the values obtained for A are

$$A=1{\cdot}526 \text{ from VII.}$$
$$A=1{\cdot}508 \text{ from VIII.}$$
$$A=1{\cdot}341 \text{ from IX.}$$

Mean value of A=1·459, and the general formula becomes

$$Q^s=1{\cdot}459a^s(a^t-1)+{\cdot}00648\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11.)$$

Comparison of Observed and Calculated Values of Q for dry *New Red Sandstone*.

Series of experiments.	Values of θ (C.).	Values of t (C.).	Calculated values of Q.	Corrected observed values of Q.	Differences.
VII.	16·22	45·86	1·44	1·47	0·03
VIII.	15·18	87·83	3·24	3·29	0·05
IX.	16·95	141·57	6·24	6·15	−0·09

18. From two series of experiments (X. and XI.) on a disc of *Sandstone* used for building purposes, I obtained the following values of A:—

$$A=1{\cdot}620 \text{ from series X.}$$
$$A=1{\cdot}475 \text{ from series XI.}$$

In X. the temperature t was = 93°·7 (C.),
In XI. the temperature t was =151°·14 (C.).

The mean value of A=1·547, and our general formula becomes

$$Q^s=1{\cdot}547a^s(a^t-1)+{\cdot}00648\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12.)$$

19. Two other series of experiments (XII. and XIII.) were made in a similar manner, with a disc of limestone, the surface of which was highly *polished*.

$$A=1{\cdot}660 \text{ from series XII.}$$
$$A=1{\cdot}513 \text{ from series XIII.}$$

Mean value of A=1·586, the value of t being

97°·65 (C.) in XII.
155°·1 (C.) in XIII.

The general formula becomes

$$Q^s=1{\cdot}586a^s(a^t-1)+{\cdot}00648\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.)$$

20. Two similar series (XIV. and XV.) were made with the same disc, the radiation taking place from its *unpolished* surface. The following values were obtained:—

$$A=2{\cdot}060 \quad . \quad . \quad . \quad . \quad t=\ 63{\cdot}5 \text{ (C.).}$$
$$A=2{\cdot}161 \quad . \quad . \quad . \quad . \quad t=125{\cdot}7 \text{ (C.).}$$

Mean value of A=2·110; and therefore

$$Q^o=2\cdot110a^t(a^t-1)+\cdot00648\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14.)$$

21. It only remains to determine the capacity for heat of the calorimeter, and so to modify the numerical values of the coefficients in the preceding formulæ as to obtain numerical values of Q in which unity shall represent the quantity of heat required to raise a given weight of distilled water *one degree Centigrade*. I shall assume this given weight to be 1000 grains.

In the first place it was necessary to determine the weight of the distilled water used in the experiments, and that of the tin vessel containing it. For this purpose the vessel was filled with water while the bulb of its thermometer was still inserted in it. The thermometer was then removed, and the vessel and contained water was found to weigh

8524 grs.

When empty and dry, the vessel itself weighed

3170·5 grs.,

and consequently the weight of water was

5353·5 grs.

The tin plate of which the vessel was formed consisted of thin sheet iron coated with tin, the weight of which was $\frac{1}{10}$th of that of the iron. Also the capacity for heat of sheet iron may be taken =·11, and that of tin =·06, the capacity of water being unity. Let w_1 and w_2 be the weights of iron and tin respectively in the tin plate, and c its capacity for heat. Then if W= the weight of the vessel,

$$w_1+w_2=W,$$

$$w_2=\frac{w_1}{10};$$

also

$$w_1=\frac{10}{11}W, \text{ and } w_2=\frac{1}{11}W,$$

and the weight of water equivalent to w_1 of iron and w_2 of tin,

$$=w_1(\cdot11)+w_2(\cdot06)$$
$$=W(\cdot1+\cdot0055)$$
$$=319 \text{ grs.}$$

Another small correction is required for the bulb of the thermometer and the small portion of the glass tube inserted within the vessel of the calorimeter, and the mercury contained in the thermometer. The volumes of the glass and mercury were carefully estimated, and thence their weights ascertained. It was then easy to estimate approximately their capacity for heat, which was found to be equal to that of about 17 grains of water. This, being added to the correction of the last paragraph, gives 336 grains as the equivalent quantity of water to be added to the 5353·5 grains contained in the

calorimeter. Hence the heat communicated to the calorimeter in each experiment may be considered to have been employed in raising by the observed amount in the observed time the temperature of 5689·5 grains of distilled water. Taking 1000 grains as the unit of weight, this weight will be represented by the number 5·6895.

Again, the time corresponding to 500 beats of the watch employed (the time to which all the experimental results were reduced) was =3·3333 minutes. Now the above quantity of water was raised Q^o in that time, or $\frac{Q^o}{3\cdot3333}$ in one minute, which we may take as the unit of time. Consequently the heat would have raised a unit of water (1000 grs.) $\frac{Q^o}{3\cdot3333}\cdot5\cdot6895$ degrees in one minute; or if Q^i denote the numerical value of the heat communicated to the calorimeter with the thermal unit above mentioned, we have

$$Q^i=Q^o\cdot\frac{5\cdot6895}{3\cdot3333}$$

$$=1\cdot706\,Q^o.$$

Also the area of the radiating surfaces was 23·758 square inches, and therefore if Q denote the quantity of heat emanating from a *square foot*,

$$Q=Q^i\cdot\frac{144}{23\cdot758},$$

$$Q^i=6\cdot060;$$

or finally,

$$Q=10\cdot338\,Q^o.$$

Hence in each of the preceding expressions for Q^o, we must multiply the numerical factor of each term by 10·338, and we shall obtain the numerical value of the quantity of heat which would emanate in *one minute* from a *square foot* of the proposed surface for any assigned value of the temperature denoted by θ (Cent.), and the difference of temperatures denoted by t (Cent.), the *unit of heat* being that heat which would raise the temperature of 1000 grains of distilled water 1° (Cent.). Our formulæ thus become for

Glass.

$$Q=9\cdot566\,a^\theta(a^t-1)+\cdot03720\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}.$$

Dry Chalk.

$$Q=8\cdot613\,a^\theta(a^t-1)+\cdot03720\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}.$$

Dry New Red Sandstone.

$$Q=8\cdot377\,a^\theta(a^t-1)+\cdot03720\left(\frac{p}{\cdot72}\right)^{\cdot45}t^{1\cdot233}.$$

Sandstone (building stone).

$$Q=8{\cdot}882\,a^{t}(a'-1)+{\cdot}03720\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}.$$

Polished Limestone.

$$Q=9{\cdot}106\,a^{t}(a'-1)+{\cdot}03720\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}.$$

Unpolished Limestone (same block).

$$Q=12{\cdot}808\,a^{t}(a'-1)+{\cdot}03720\left(\frac{p}{{\cdot}72}\right)^{{\cdot}45}t^{1{\cdot}233}.$$

The approximate equality of the different values of Q for these substances under similar conditions, is what would have scarcely been anticipated. The value of Q, however, for the surface of silver, as shown by DULONG and PETIT, is very much smaller than the preceding values. Such appears also to be the case with mercury and polished steel. But in this last case the surface of the steel and its radiating power are affected by high temperatures, at which also an amount of vaporization takes place from the surface of mercury, which affects the indications of the instrument.

XXII. *Contributions to the History of the Phosphorus-Bases.*

By AUGUSTUS WILLIAM HOFMANN, *F.R.S.*

Received June 21,—Read June 21, 1860.

FIRST MEMOIR.

IN a paper* published a few years ago by M. CAHOURS and myself, the remarkable phosphorus-compounds, whose existence was first pointed out by the experiments of M. PAUL THÉNARD, were subjected to a more complete examination than they had previously received.

The discovery of a better mode of preparation enabled us to gain a clearer view of the nature of this group of substances, and to throw additional light on their relations to the nitrogen-bases; but, owing to the overwhelming number of reactions which presented themselves, we were unable to submit the behaviour of the phosphorus-bases with other groups of bodies to a detailed examination.

In continuation of former experiments, I have lately been much engaged in the investigation of the polyatomic ammonias, the study of which was naturally suggested by the beautiful researches which have been published on the polyatomic alcohols. In the course of these experiments, I frequently had occasion to return to the phosphorus-bases, the employment of triethylphosphine in particular having in many instances led to results which would not easily have been obtained in any other way. The possibility of preparing this body in a state of perfect purity and in considerable quantity, by a series of processes, which, if not quite simple, are at least definite and certain, its position in the system of organic compounds, its conveniently situated boiling-point, the energy and precision of its reactions, and lastly, the simplicity which characterizes these reactions, in consequence of the absence of unreplaced hydrogen in triethylphosphine, —whereby the formation of a large number of compounds of subordinate theoretical interest is excluded,—all these conditions tend strongly to invite us to the study of a body, in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness.

It was originally my intention to put together—in one frame, as it were—the various facts which I have collected relating to the phosphorus-bases; but the material lies scattered in so many directions, that I deem it more advisable to publish these observations in a number of shorter memoirs, which, from the nature of the subject, must be more or less fragmentary.

* Philosophical Transactions, vol. cxlvii. p. 575.

Preparation of Triethylphosphine.

The whole of the material used in my experiments was prepared by the process formerly described in detail by Cahours and myself. The only alteration, which has been found advisable, relates to the separation of the triethylphosphine from the chloride-of-zinc-compound, which is produced by the action of trichloride of phosphorus on zinc-ethyl. It was formerly our practice to throw solid hydrate of potassium into the viscid mass of this salt, and then to dissolve the potassa by gradually dropping water into the retort, the heat resulting from the reaction being sufficient to carry over the base nearly anhydrous. It is better, however, to mix the double salt at once with water, and then decompose it in a retort filled with hydrogen, by allowing strong potassa-solution slowly to flow into it. On subsequently distilling the mixture on a sand-bath in a continuous but very slow stream of hydrogen, the triethylphosphine passes over with the aqueous vapour and floats on the top of the condensed water in the receiver. By adopting this mode of proceeding, the reaction is more under the command of the operator, and as the phosphorus-base is not sensibly soluble in water, the quantity of the product is not thereby diminished.

By exact adherence to the prescribed conditions, it is by no means difficult to prepare considerable quantities of pure triethylphosphine; nevertheless the amount obtained is always less than it should be in proportion to the weight of the materials used. This loss is mainly due to the formation of secondary products, which cannot be wholly avoided even when the zinc-ethyl is carefully prepared, and to partial decomposition of the latter substance during distillation: for it is scarcely possible to imagine a more elegant reaction than that which takes place between trichloride of phosphorus and ready-formed zinc-ethyl. Under these circumstances, many attempts were naturally made to obtain the phosphorus-base in other ways; I have always, however, returned to our original process.

Totally unsuccessful was the attempt to obtain triethylphosphine, without previous preparation of zinc-ethyl, by exposing a mixture of 1 equiv. of trichloride of phosphorus and 3 equivs. of iodide of ethyl with excess of zinc in sealed tubes to a temperature of 150° C. The bodies react under these circumstances; but as only traces of triethylphosphine are produced, I have not thought it worth while to pursue this reaction further. A more favourable result was obtained by heating a mixture of zinc and phosphorus with anhydrous iodide of ethyl to between 150° and 160°. After several hours' digestion, the tubes were found to be coated with white crystals, and a considerable portion of the phosphorus had passed into the red modification. Powerful escape of gas always took place on opening the tubes, and in several instances they were shattered, even when their points were softened in the lamp-flame to diminish the violence of the concussion. Besides zinc-ethyl, the presence of which is indicated by the abundant evolution of hydride of ethyl which is observed on treating the contents of the tube with water, the chief products of this reaction are three phosphorus-compounds, which are formed in proportions varying according to the temperature and the duration of the action.

On extracting the brown residue in the tubes with warm water, and evaporating the clear solution, an oily substance separates which covers the bottom of the dish, and on cooling solidifies into a mass of hard crystals. By repeatedly crystallizing this substance from boiling water and from alcohol, large crystals are obtained, which give off triethylphosphine when treated with potassa even in the cold, and are found to consist of a compound of iodide of zinc with iodide of triethylphosphonium.

I. 0·3721 grm. of the compound dried at 100°, when burnt with a mixture of chromate of lead and oxide of copper*, gave 0·2435 grm. of carbonic acid and 0·1320 grm. of water.

II. 0·3274 grm. of substance gave 0·3789 grm. of iodide of silver.

III. 0·3800 grm. of substance gave 0·4370 grm. of iodide of silver.

These experiments lead to the formula

$$C_6H_{16}PZnI_2 = [(C_2H_5)_3HP]I, ZnI\dagger.$$

	Theory.		Experiment.		
			I.	II.	III.
C_6	72	17·75	17·85	——	——
H_{16}	16	3·95	3·94	——	——
P	31	7·65	——	——	——
Zn	32·5	8·01	——	——	——
I_2	254	62·64	——	62·52	62·13
	405·5	100·00			

A solution of iodide of triethylphosphonium mixed with iodide of zinc immediately gives a crystalline compound of exactly similar characters.

The mother-liquor of the double salt yields, when further evaporated, another crystalline body which is more difficult to purify. After three or four crystallizations, however, well-developed crystals are obtained, which do not yield triethylphosphine when treated with potash, either in the cold or with aid of heat. The analysis, to be given further on, shows that this crystalline substance is a compound of iodide of zinc and oxide of triethylphosphine,

$$C_6H_{15}PO, ZnI = (C_2H_5)_3PO, ZnI.$$

The third compound, which remains in the mother-liquor after the two former have crystallized out, and separates, on further evaporation, in beautiful needle-shaped crystals, may be recognized without difficulty as iodide of tetrethylphosphonium. The crystals are insoluble in cold potassa-solution, and give off triethylphosphine only when heated with solid hydrate of potassium.

* The combustion of the phosphorus-compounds is not very easily effected. The experiment succeeds best with a mixture of chromate of lead and oxide of copper. All the carbon-determinations quoted in the following pages have been made with this mixture, unless another mode of proceeding is specially stated. All the substances analysed were dried at 100°, except in a few cases, when the mode of drying is also specially mentioned.

† H=1; O=16; S=32; C=12.

This iodide likewise unites with iodide of zinc; and as this latter salt is always present in the mother-liquor in considerable quantity, the double salt is generally obtained together with the simple iodide.

The mode of formation of these compounds is represented by the following equations:—

$$8C_2H_5I + P_2 + 3Zn_2 = 2([(C_2H_5)_3HP]I, ZnI) + 4ZnI + 2C_2H_4.$$

$$8C_2H_5I + P_2 + 3Zn_2 = 2([(C_2H_5)_4P]I, ZnI) + 4ZnI.$$

The compound containing oxide of triethylphosphine is evidently formed at the expense of the air in the tube:—

$$2[(C_2H_5)_3P] + O_2 + 2ZnI = 2[(C_2H_5)_3PO, ZnI].$$

The above zinc-iodide-compounds of triethyl- and tetrethyl-phosphonium possess interest only in so far as they may serve for the preparation of the phosphorus-base. The mixture evaporated to dryness and distilled with hydrate of potassium in an atmosphere of hydrogen, does indeed yield appreciable quantities of triethylphosphine: the action of iodide of ethyl upon a mixture of zinc and phosphorus may therefore be recommended when it is desired to prepare a sample of this remarkable compound without specially arranged apparatus; but it is not adapted for the preparation of the phosphorus-base on the large scale.

I have endeavoured to prepare by this process *triamylphosphine* and *triallylphosphine*, but the results were not such as to encourage me to continue the experiments.

Cahours has recently made similar experiments, but with a difference in the mode of conducting them, which cannot fail to influence the result. Instead of subjecting iodide of ethyl to the action of a mechanical mixture of zinc and phosphorus, he has caused the compound Zn_3P to act upon iodide of ethyl at a high temperature. The reaction will doubtless proceed more regularly under these conditions; but the advantage which may perhaps be gained by avoiding the preparation of the zinc-ethyl is compromised, at least in part, by the time and trouble expended in the somewhat complicated preparation of trizincophosphide.

Oxide of Triethylphosphine.

The formation of the compound of this oxide with iodide of zinc to which I have alluded, induced me to subject to a careful examination the beautifully crystallized body produced from the phosphorus-base by exposure to the air. In our former experiments, Cahours and myself had often observed this substance, but we did not succeed in obtaining it in a state of purity fit for analysis. Nevertheless, founding our conclusion on the composition of the corresponding sulphur-compound, and having regard to the analogies presented by the bodies of the arsenic- and antimony-series, we regarded this body as the oxide of the phosphorus-base

$$(C_2H_5)_3PO.$$

I have since confirmed this formula by analysis.

The difficulties which in our experiments opposed the preparation of this compound in the pure state, arose entirely from the comparatively small quantity of material with which we had to work. Nothing is easier than to obtain this oxide in a state of purity, provided the available quantity of material is sufficient for distillation. In the course of a number of preparations of triethylphosphine for the new experiments, a considerable quantity of the oxide had accumulated in the residues left after distilling the zinc-chloride-compound with potassa. On subjecting these residues to distillation in a copper retort, a large portion of the oxide passed over with the aqueous vapours, and a further quantity was obtained as a tolerably anhydrous but strongly coloured liquid, by dry distillation of the solid cake of salts which remained after all the water had passed over. The watery distillate, with or without addition of hydrochloric acid, was evaporated on the water-bath as far as practicable, and the concentrated solution was mixed with solid hydrate of potassium, which immediately separated the oxide in the form of an oily layer floating on the surface of the potash. The united products were then left in contact with solid potash for twenty-four hours, and again distilled. The first portion of the distillate still contained traces of water, a thin layer of triethylphosphine floating upon the surface. As soon as the distillate solidified, the receiver was changed, and the remaining portion (about nine-tenths) collected apart as the pure product. To prevent absorption of water, the quantity required for analysis was collected during the distillation.

0·2589 grm. of oxide of triethylphosphine gave 0·5098 grm. of carbonic acid and 0·2660 grm. of water.

The formula

$$C_6H_{15}PO=(C_2H_5)_3PO$$

requires the following values:—

	Theory.		Experiment.
C_6	72	53·73	53·70
H_{15}	15	11·20	11·41
P	31	23·13	——
O	16	11·94	——
	134	100·00	

With reference to the properties of oxide of triethylphosphine, I may add the following statements to the description formerly given*. This substance crystallizes in beautiful delicate needles, which, if an appreciable quantity of the fused compound be allowed to cool slowly, frequently attain the length of several inches. I have been unable to obtain well-formed crystals; as yet I have not found a solvent from which this substance can be crystallized. It is soluble in all proportions, both in water and alcohol, and separates from these solvents on evaporation in the liquid condition, and solidifies only after every trace of water or alcohol is expelled. Addition of ether to the alcoholic solution precipitates this body likewise as a liquid. The melting point of oxide

* Philosophical Transactions, 1857, p. 586.

of triethylphosphine is 44°; the point of solidification at the same temperature. It boils at 240° C. (corrected).

As no determination of the vapour-density of any member of the group of compounds to which the oxide of triethylphosphine belongs has yet been made, it appeared to me of some interest to perform this experiment with the oxide in question. Since the determination by DUMAS' method could not have been performed without sacrificing a considerable amount of material, and GAY-LUSSAC's was inapplicable on account of the high boiling-point of the compound, I adopted a modification of the latter, consisting essentially in generating the vapour in the closed arm of a U-shaped tube filled with mercury and immersed in a copper vessel containing heated paraffin, and calculating its volume from the weight of the mercury driven out of the other arm. As I intend to publish a full description of this method, which promises to be very useful in certain cases, I shall here content myself with stating the results obtained in one of the experiments.

Substance	0·150 grm.
Volume of vapour	49·1 cub. cent.
Thermometer (corrected)	266°·6 C.
Barometer at 0° C.	0·7670 metre.
Additional mercury column at 0° C. . .	0·1056 metre.

These numbers prove the vapour-density of oxide of triethylphosphine to be 66·30, referred to hydrogen as unity, or 4·60 referred to atmospheric air. Assuming that the molecule of oxide of triethylphosphine corresponds to 2 vols. of vapour*, the calculated specific gravity of its vapour $=\frac{134}{2}=67$, when referred to hydrogen, and 4·63 when referred to air. Hence we may conclude that in oxide of triethylphosphine, the elements are condensed in the same manner as in the majority of thoroughly investigated organic compounds.

From the facility with which triethylphosphine is converted into the oxide by exposure to the air, even at ordinary temperatures, and from the very high boiling-point of the resulting compound, in consequence of which its vapour can exert but a very slight tension at ordinary temperatures, I am induced to think that the phosphorus-base may be used in many cases for the volumetric estimation of oxygen. When a paper ball soaked in triethylphosphine is passed up into a portion of air confined over mercury, the mercury immediately begins to rise, and continues to do so for about two hours, after which the volume becomes constant, the diminution corresponding very nearly to the proportion of oxygen in the air. To obtain very exact results, however, it would probably be necessary in every case to remove the residual vapour of triethylphosphine by means of a ball saturated with sulphuric acid.

Oxide of triethylphosphine exhibits in general but small tendency to unite with other bodies; nevertheless it forms crystalline compounds with iodide and bromide of zinc. I have examined more particularly the zinc-iodide-compound already mentioned.

* H_2O=2 vols. of vapour.

Oxide of Triethylphosphine and Iodide of Zinc.

On mixing the solutions of the two bodies, the compound separates, either as a crystalline precipitate or in oily drops, which soon solidify with crystalline structure. It is easily purified by recrystallization from alcohol.

I. 0·6535 grm. of the double salt gave 0·5884 grm. of carbonic acid and 0·3070 grm. of water.

II. 0·3685 grm. of the double salt gave 0·3299 grm. of carbonic acid and 0·1757 grm. of water.

III. 0·5985 grm. of the salt obtained in the same preparation gave 0·4782 grm. of iodide of silver.

IV. 1·1680 grm. of another preparation gave 0·9420 grm. of iodide of silver.

V. 0·3060 grm. of the double salt gave 0·2466 grm. of iodide of silver. The crystals used in this analysis had been obtained by the action of zinc and phosphorus on iodide of ethyl.

VI. 0·5456 grm. of substance gave 0·4333 grm. of iodide of silver.

VII. 1·1600 grm. of substance gave 0·9340 grm. of iodide of silver.

The salt employed in analyses VI. and VII. had been prepared by precipitating the hydrochloric solution of the oxide with iodide of zinc.

These analytical results establish the formula

$$C_6H_{15}PO, ZnI = (C_2H_5)_3PO, ZnI.$$

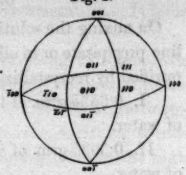
	Theory.		Experiment.						
			I.	II.	III.	IV.	V.	VI.	VII.
C_6	72	24·53	24·55	24·39	——	——	——	——	——
H_{15}	15	5·12	5·22	5·29	——	——	——	——	——
P	31	10·56	——	——	——	——	——	——	——
O	16	5·45	——	——	——	——	——	——	——
Zn	32·5	11·08	——	——	——	——	——	——	——
I	127	43·26	——	——	43·17	43·53	43·55	42·92	43·51
	293·5	100·00							

It is remarkable that this compound is formed in presence of a large excess of hydriodic and even of hydrochloric acid.

The crystals melt at 99°; they readily dissolve in warm water, and even more easily in alcohol. From the alcoholic solution well-formed crystals are frequently obtained.

My friend Quintino Sella has examined these crystals. This examination, as well as all the other crystallographical researches given in these papers, are parts of inquiries to which the celebrated crystallographer of Turin is devoting such leisure as is left to him by numerous professorial avocations and the onerous duties of an active parliamentary life. To his kindness I am indebted for the following description:—

Fig. 1.



"System monoclinic:—

100, 101=34° 25′; 101, 001=48° 48′; 111, 010=50° 16′.

Forms observed:—

100, 010, 001, 110, 011, 111 (Fig. 1).

Angles.	Calculated.	Observed. In hemitropic crystals.	Observed. In simple crystals.
	° ′	° ′	° ′
100, 010 =	90	——	——
100, 001 =	83 13	82 57	83 23
100, 110 =	47 39	47 48	47 42
100, 011 =	86 10	86 10	——
100, 111 =	50 37	50 21	——
010, 001 =	90	——	——
010, 110 =	42 21	——	42 19
010, 011 =	34 24	——	——
010, 111 =	50 16	——	——
001, 110 =	85 26	85 18	85 23
001, 011 =	55 36	55 44	——
001, 111 =	59 34	59 39	——
110, $\bar{1}$10 =	84 42	84 29	84 38
110, 011 =	52 45	——	——
110, 01$\bar{1}$ =	61 55	——	——
110, 111 =	25 52	25 30	——
110, $\bar{1}$1$\bar{1}$ =	87 49	——	——
011, 01$\bar{1}$ =	68 48	68 32	——
011, 111 =	35 33	35 44	——
011, $\bar{1}$1$\bar{1}$ =	76 3	——	——
111, $\bar{1}$1$\bar{1}$ =	100 32	100 37	——

According to Naumann:—

$a : b : c = 1{\cdot}3312 : 1 : 0{\cdot}9052$; $\gamma = 83° 13'$.

Forms observed:—

$\infty \breve{P} \infty$, $\infty \breve{P} \infty$, $0P$, ∞P, $\breve{P} \infty$, $-P$.

According to Weiss:—

$a : b : c = 1 : 0{\cdot}9052 : 1{\cdot}3312$; $a \circ c = 96° 47'$.

Forms observed:—

$a:\infty b:\infty c$; $\infty a:b:\infty c$; $\infty a:\infty b:c$; $a:b:\infty c$; $\infty a:b:c$; $a:b:c$.

According to Levy:—

$$M\,M=84^\circ\,42'; \quad M\,P=94^\circ\,34'; \quad b:h=1:0{\cdot}9869.$$

Forms observed:—

h^1, g^1, P, M, e^1 $d^{\frac{1}{2}}$.

Combinations observed:—

110, 001 (Fig. 2).
110, 001; 100 (Figs. 3 & 4).
110, 001; 100, 010 (Fig. 5).
001, 100, 110, 111.
001, 100, 110, 111; 011.
001, 100, 110, 111; 011, 010 (Fig. 6).

Fig. 2.

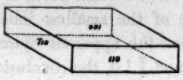


Fig. 3.

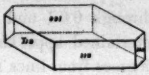


Fig. 4.

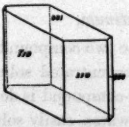


Fig. 5.

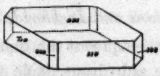
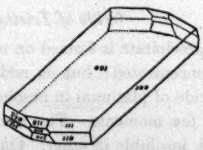


Fig. 6.



Hemitropic crystals with the axis of hemitropy [1 0 0], with the face of hemitropy 0 0 1=0 P (Naumann)=$\infty a:\infty b:c$ (Weiss)=P (Levy).

Fig. 7.

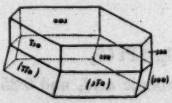


Fig. 8.

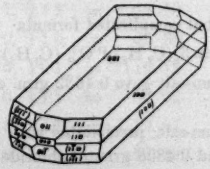
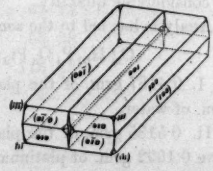


Fig. 9.



The hemitropic crystals are sometimes simple, as in Fig. 7; sometimes complicated, as in Fig. 8. It is then difficult to distinguish them from trimetric crystals; they become, however, intelligible by assuming that they result from four hemitropic crystals

grouped round [1 0 0], as in Fig. 9. It is found sometimes that several crystals, like those of Fig. 8, are associated by 0 0 1.

It deserves to be noticed that the crystals (Figs. 2, 3, 4, 5 and 7) were formed in the presence of hydrochloric acid, and that in the absence of this acid, only crystals of Fig. 8 are obtained, which, without the study of the cleavage and the optical characters, could not be distinguished from trimetric crystals.

Cleavages 0 0 1 and 1 1 0 distinct and easily obtained. The cleavage 1 1 0 of the hemitropic crystals (Fig. 8) exhibits re-entering angles.

Lustre vitreous on the fracture, fatty on the faces.

Hardness somewhat greater than that of gypsum.

The crystals are optically positive; the line of symmetry [0 1 0] is their principal medium line. The coloured rings are visible through the faces of the cleavage 1 1 0, and the plane of the optical axes appears to be perpendicular to the axis of the prism 1 1 0. Through the cleavage 1 1 0 of the hemitropic crystals (Fig. 7), two systems of rings are seen.

The angle of the optical axes, seen through the faces 1 1 0 and $\bar{1}$ 1 0, is 74°. By rough measurement through 0 0 1 and 0 1 $\bar{1}$, the value of the smallest index of refraction $\gamma = 1{\cdot}58$ was determined approximately; and since the apparent optical axes deviate only by a few degrees from lines normal to 1 1 0 and $\bar{1}$ 1 0, the conclusion is admissible that the internal angle of the optical axes differs but little from 78°*."

Oxide of Triethylphosphine and Dichloride of Platinum.

No precipitate is formed on mixing the aqueous solutions of the two compounds, however concentrated; but on adding the anhydrous oxide to a concentrated solution of dichloride of platinum in absolute alcohol, a crystalline platinum-compound is deposited after a few moments. This compound is exceedingly soluble in water, easily soluble in alcohol, insoluble in ether. On adding ether to the alcoholic solution, the salt is precipitated, although with difficulty, in the crystalline state. The alcoholic solution, when evaporating spontaneously, yields beautiful hexagonal plates, frequently of rather large dimensions. On account of its extreme solubility, it is not quite easy to obtain this salt in considerable quantity.

Analysis has led to the somewhat complicated formula

$$C_{24}H_{60}P_4O_3Pt_2Cl_6 = 3[(C_2H_5)_3PO], (C_2H_5)_3PCl_2, 2PtCl_2.$$

I. 0·4187 grm. of the platinum-salt gave 0·4632 grm. of carbonic acid, and 0·2545 grm. of water.

II. 0·5185 grm. of the platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0·1092 grm. of platinum, and 0·4808 grm. of chloride of silver.

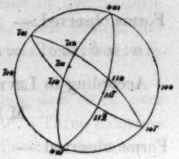
* Some of Sella's crystallographical researches were received whilst this paper was passing through the press. These researches will be published in detail in *Memorie della Reale Accademia delle Scienze di Torino*, Serie 2. tom. xx. under the title: *Sulle Forme Cristalline di alcuni Sali derivati dall' Ammoniaca per* Quintino Sella, *Deputato al Parlamento Italiano.*

The above formula requires:—

	Theory.		Experiment.	
			I.	II.
C_{24}	288	30·95	30·17	——
H_{60}	60	6·45	6·75	——
P_4	124	13·33	——	——
O_3	48	5·16	——	——
Pt_2	197·4	21·21	——	21·06
Cl_6	213	22·90	——	22·93
	930·4	100·00		

The platinum-salt has likewise been examined by QUINTINO SELLA.

Fig. 10.



"System monoclinic:—

100, 101=27° 19′; 101, 001=46° 23′; 010, 111=41° 4′.

Forms observed:—

100, 001, 110, $\bar{1}01$, $\bar{1}11$, $\bar{1}12$ (Fig. 10).

Angles.		Calculated.	Observed.
100, 001	=	73° 42′	73° 30′
100, 110	=	56 41	——
100, $\bar{1}01$	=	143 30	——
100, $\bar{1}11$	=	116 36	——
100, $\bar{1}12$	=	108 9	——
001, 110	=	81 8	81 8
001, $\bar{1}01$	=	69 48	69 48
001, $\bar{1}11$	=	78 55	78 51
001, $\bar{1}12$	=	61 10	61 14
110, $\bar{1}10$	=	66 38	66 38
110, $\bar{1}01$	=	116 12	116 23
110, $\bar{1}11$	=	63 22	——
110, $11\bar{1}$	=	19 57	——
110, $\bar{1}12$	=	63 19	——
110, $11\bar{2}$	=	37 42	——
$\bar{1}01$, $\bar{1}11$	=	56 9	——
$\bar{1}01$, $\bar{1}12$	=	52 53	52 32

Angles.		Calculated.
$\bar{1}11, 11\bar{1}$	=	67° 42′
$\bar{1}11, \bar{1}12$	=	17 44
$\bar{1}11, 11\bar{2}$	=	73 43
$\bar{1}12, 11\bar{2}$	=	84 11

According to Naumann:—

$$a:b:c=1{\cdot}5776:1:0{,}6308; \quad \gamma=73° 42'.$$

Forms observed:—

$$\infty\breve{P}\infty, \quad 0P, \quad \infty P, \quad \breve{P}\infty, \quad P, \quad \tfrac{1}{2}P.$$

According to Weiss:—

$$a:b:c=1:0{\cdot}6308:1{\cdot}5776; \quad a\,o\,c=106° 28'.$$

Forms observed:—

$$a:\infty b:\infty c; \quad \infty a:\infty b:c; \quad a:b:\infty c; \quad -a:\infty b:c; \quad -a:b:c; \quad -a:b\ \tfrac{1}{2}c$$

According to Levy:—

$$M\,M=66° 38'; \quad M\,P=98° 52'; \quad b:h=1:1{\cdot}3343.$$

Forms observed:—

$$h', \quad P, \quad M, \quad a', \quad b^{\frac{1}{2}}, \quad b'.$$

Combinations observed:—

0 0 1, 1 0 0, 1 1 0 (Fig. 11).

0 0 1, 1 1 0, $\bar{1}$ 1 2, $\bar{1}$ 0 1.

0 0 1, 1 1 0, $\bar{1}$ 1 2, $\bar{1}$ 0 1, 1 0 0, $\bar{1}$ 1 1 (Fig. 12).

Fig. 11.

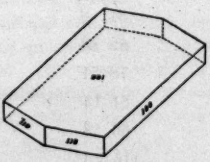
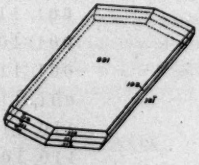


Fig. 12.



Cleavages $\bar{1}$01 and 110 distinct and easily obtained.

Colour orange-red.

The optical axes are situated in 0 1 0, *i. e.* in the plane of symmetry. They are seen through the faces 0 0 1 and the cleavages $\bar{1}$ 0 1, and they make an apparent angle of about 64°."

On mixing a concentrated solution of the oxide of triethylphosphine with *trichloride*

of gold, a deep-yellow oil is separated, which crystallizes with difficulty after considerable standing. This compound is exceedingly soluble in water and in alcohol. When the aqueous solution is heated, the gold is reduced; the transformation which the oxide of triethylphosphine undergoes in this reaction has not been examined.

Chloride of Tin forms likewise an oily compound with the oxide: I have not succeeded in crystallizing this compound.

Chloride of Mercury is without any action on oxide of triethylphosphine.

Oxychloride of Triethylphosphine.

On passing a current of dry hydrochloric acid through a layer of oxide of triethylphosphine which is fused in a U-shaped tube surrounded by boiling water, brilliant crystals are soon formed. These crystals, however, rapidly disappear, the compound formed in the commencement of the reaction uniting with an excess of hydrochloric acid. The viscous liquid, which ultimately remains behind, loses, when heated, the excess of hydrochloric acid, leaving an exceedingly deliquescent crystalline mass, very soluble in alcohol, insoluble in ether.

For analysis, the new compound was washed with absolute ether, and dried over sulphuric acid *in vacuo*, either at the common temperature or at 40°. Three chlorine-determinations in specimens of different preparations yielded the following results:—

I. 0·8845 grm. of substance gave 0·6920 grm. of chloride of silver.
II. 0·3548 grm. of substance gave 0·2918 grm. of chloride of silver.
III. 0·3557 grm. of substance gave 0·2979 grm. of chloride of silver.

The chlorine-percentages corresponding to these numbers exhibit far greater discrepancies than are generally observed in experiments of this description; this result is obviously due to the extremely deliquescent character of the crystals. It cannot, however, be doubted that the compound examined is an oxychloride of triethylphosphine represented by the formula

$$C_{12}H_{30}P_2OCl_2=(C_2H_5)_3PO+(C_2H_5)_3PCl_2.$$

	Theory.		Experiment.		
			I.	II.	III.
2 equivs. Triethylphosphine	236	73·07	——	——	——
1 equiv. Oxygen	16	4·95	——	——	——
2 equivs. Chlorine	71	21·98	19·35	20·35	20·72
1 equiv. Double Compound	323	100·00			

The dichloride of triethylphosphine cannot be formed by the action of hydrochloric acid upon the oxide.

The oxychloride exhibits with other compounds the deportment of the oxide. It furnishes with dichloride of platinum the same platinum-salt which is obtained with

the oxide. In a similar manner, it gives with iodide of zinc the iodide-of-zinc-compound of the oxide previously described. Only once—under conditions not sharply enough observed at the time, and which I was afterwards unable to reproduce in repeated experiments—a compound of the oxychloride with iodide of zinc was formed. This substance, readily soluble in water and alcohol, crystallized from the latter solvent in beautiful colourless transparent octohedra, which, on analysis, gave the following result:—

0·2093 grm. of salt, precipitated by nitrate of silver, gave 0·2474 grm. of a mixture of iodide and chloride of silver.

With the probable assumption that the compound contains 1 equiv. of chlorine for 1 equiv. of iodine, this result corresponds to 50·74 per cent. of chlorine and iodine.

Accordingly the octohedra would be a double compound of the iodide-of-zinc-salts of the oxide and of the chloride of triethylphosphine.

The formula

$$C_{12}H_{30}P_2OCl_2Zn_2I_2=(C_2H_5)_3PO,\ ZnI+(C_2H_5)_3PCl_2,\ ZnI$$

requires 50·62 per cent. of chlorine and iodine.

Behaviour of Triethylphosphine with Sulphur-compounds.

The remarkable tendency of the phosphorus-base to unite with sulphur has already been mentioned in the previous memoir; the combination of the two bodies is attended with evolution of heat, the result being a beautifully crystalline substance,

$$C_6H_{15}PS=(C_2H_5)_3PS,$$

corresponding to the oxide of triethylphosphine.

This behaviour has induced me to study the action of several sulphur-compounds on the phosphorus-base. In the cases which I have examined, the ultimate product is almost invariably the sulphide of triethylphosphine, already mentioned as resulting from the direct combination of the phosphorus-base with sulphur; but the conditions under which this sulphide is produced vary considerably, and in the majority of cases it occurs only as a secondary product of the decomposition of other more direct compounds, some of which appeared to me sufficiently interesting to deserve more minute investigation.

In the course of the experiments which I am going to describe, I have prepared considerable quantities of the sulphide of triethylphosphine. This compound, although remarkable for the facility with which it crystallizes, is not easily procured in well-formed crystals. It was only once or twice that I obtained crystals with good faces. They were examined by Quintino Sella, who communicates to me the following results:—

"System rhombohedric:—

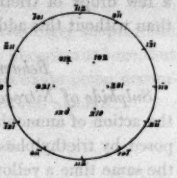
$$100,\ 111=54°\ 35'.$$

Forms observed:—

$$10\bar{1},\ 2\bar{1}\bar{1},\ 210$$ (Fig. 13).

Angles.	Calculated.	Observed.
$10\bar{1}, 01\bar{1}$	= 60° 0′	60° 1′
$10\bar{1}, 2\bar{1}\bar{1}$	= 30 0	29 59
$10\bar{1}, 210$	= 50 56	51 0
$10\bar{1}, 120$	= 71 38	71 34
$2\bar{1}\bar{1}, 210$	= 56 55	——
$2\bar{1}\bar{1}, 120$	= 90 0	——
$210, 120$	= 36 44	36 50
$210, 021$	= 66 10	66 20
$210, 012$	= 78 9	——

Fig. 13.



According to NAUMANN:—

R=90° 13′.

Forms observed:—

∞P 2, ∞R, $\frac{3}{5}$P 2.

According to WEISS:—

a=0·8211.

Forms observed:—

$a:\frac{1}{2}a:a:\infty c$; $\infty a:a:a:\infty c$; $a:\frac{1}{2}a:a:\frac{1}{3}c$.

Fig. 14.

According to LEVY:—

P P=90° 13′.

Forms observed:—

d', e^3, b^3.

Combinations observed:—

$10\bar{1}$, 210 (Fig. 14).

$10\bar{1}$, 210; $2\bar{1}\bar{1}$.

The summit of the hexagonal prisms is almost always badly terminated, since they are frequently hollow: bright faces 210 are but rarely met with. In one single case $2\bar{1}\bar{1}$ could be distinctly traced. The general habitus of the crystals is that of thin, long, hexagonal needles. At summer heat, the crystals are very soft and flexible; they may be bent 180° without breaking. At lower temperatures, they are harder and much less flexible.

The crystals are optically positive. It is possible to measure the deviation through the faces of the hexagonal prism, whence it may be inferred that the index of refraction for the extraordinary ray ϵ=1·65, and for the ordinary ray ω=1·59."

Behaviour of Triethylphosphine with Sulphuretted Hydrogen.

The phosphorus-base has no action on *sulphuretted hydrogen*. When it is brought in contact with hydrosulphuric acid over mercury, the gas does not exhibit any alteration. No sulphide of triethylphosphine is formed even in presence of air, as might indeed have been expected. The attraction of the phosphorus-base for oxygen prevents the oxida-

tion of the sulphuretted hydrogen; a solution of this gas in water, when mixed with a few drops of triethylphosphine, may be preserved in air-filled vessels much longer than without this addition.

Behaviour of Triethylphosphine with Sulphide of Nitrogen.

Sulphide of Nitrogen, N_2S_2 (?), prepared as recommended by Fordos and Gelis, viz. by the action of ammonia on chloride of sulphur dissolved in disulphide of carbon, is decomposed by triethylphosphine, with evolution of light and heat. Gas is evolved, and at the same time a yellowish liquid is produced, which, on cooling, solidifies into a fibrous mass of crystals of the sulphide.

Behaviour of Triethylphosphine with Mercaptan.

When these two bodies are mixed together in an atmosphere of carbonic acid, no alteration takes place even if they are left in contact for some time, or if they are heated to 100° in sealed tubes for twenty-four hours. But if the mixture be poured into an air-filled flask, crystals of sulphide of triethylphosphine make their appearance in a few hours. The crystals increase if the air has free access to the mixture; but if the flask be corked, the crystallization is interrupted. On opening the flask, the entry of the air may be recognized by the light cloud which the phosphorus-base, diffused through the atmosphere of the vessel, forms with the oxygen. When a mixture containing excess of mercaptan was left for a few days in an open flask, every trace of phosphorus-base had disappeared, and the remaining colourless liquid was filled with crystals of the sulphide. On mixing this liquid with water, it separated into two layers, the upper of which quickly solidified, especially on exposure to the air, to an imperfectly crystalline mass, easily recognized as a mixture of sulphide of triethylphosphine with excess of mercaptan. The impure crystals were exposed for a while to the air and then recrystallized from boiling water.

0·3703 grm. of the crystals, dried over sulphuric acid *in vacuo*, gave 0·6485 grm. carbonic acid and 0·3304 water.

The formula

$$C_6H_{15}PS=(C_2H_5)_3PS$$

requires—

		Theory.	Experiment.
C_6	72	48·00	47·76
H_{15}	15	10·00	9·91
P	31	20·67	——
S	32	21·33	——
	150	100·00	

The lower stratum of liquid is aqueous alcohol containing small quantities of oxide of triethylphosphine and mercaptan. To remove the latter, the liquid was shaken up with recently precipitated mercuric oxide and distilled. The distillate, rectified several times

over lime, yielded a clear liquid, which burnt with a colourless flame and exhibited all the characters of alcohol.

The interpretation of this result appears at the first glance exceedingly simple; the sulphide of triethylphosphine cannot be formed directly from the phosphorus-base, but owes its origin to the oxide first produced by the action of air, this oxide being decomposed by the mercaptan and yielding sulphide of triethylphosphine and alcohol:

$$(C_2H_5)_3PO+\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S=\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O+(C_2H_5)_3PS.$$

Experiment shows, however, that this equation illustrates only the final result of the reaction. Oxide of triethylphosphine and mercaptan, brought together under the most various conditions at ordinary temperatures and under pressure, do not yield a trace of sulphide of triethylphosphine; and we have to suppose, therefore, that the mercaptan interchanges its sulphur with the oxygen of the oxide of triethylphosphine, only at the instant of formation of the latter, or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

In connexion with this subject, various attempts were made to replace the oxygen in oxide of triethylphosphine by sulphur. But neither by treatment with sulphide of ammonium, nor by continued boiling with the higher sulphides of potassium, could the oxide be converted into the corresponding sulphide, whereas the conversion of the sulphide into the oxide takes place without any difficulty. This, however, is not more than might have been expected from the behaviour of the oxide with hydrochloric acid, mentioned in one of the preceding paragraphs. The different degrees of stability which characterize the oxide and the sulphide of triethylphosphine may also be strikingly seen in the behaviour of these compounds with sodium, the sulphide being reduced, with the greatest facility, to free triethylphosphine, even below the melting-point of the sodium, whereas the oxide may be distilled from sodium without experiencing the slightest alteration*. Ebullition with ordinary concentrated nitric acid likewise converts the sulphide into the oxide, the sulphur being at the same time transformed into sulphuric acid. The liquid filtered off from the precipitate obtained by barium-salts, when evaporated to dryness and fused with nitrate of potassium, yields no further trace of sulphur.

Behaviour of Triethylphosphine with Disulphide of Carbon.

These two bodies, when mixed in the anhydrous state, act upon one another with considerable force, amounting frequently to explosive violence, and unite into a red crystalline mass. The compound is best prepared by mixing the solutions of its constituents in alcohol or ether: the new body then instantly separates in beautiful red crystalline laminæ.

* In the previous memoir, it is stated that the phosphorus-base is reproduced from the oxide by the action of metallic sodium. Probably the oxide used in the former experiments contained a small quantity of free triethylphosphine, and thus led to an erroneous statement.

Several times recrystallized from alcohol and dried over sulphuric acid, the new body has furnished the following results on analysis:—

I. 0·3610 grm. of the disulphide-of-carbon-compound gave 0·5750 grm. of carbonic acid and 0·2490 grm. of water.

II. 0·3595 grm. of a new preparation gave 0·5790 grm. of carbonic acid and 0·2481 grm. of water.

III. 0·4180 grm. of a third preparation gave 0·6680 grm. of carbonic acid and 0·3027 grm. of water.

IV. 0·3505 grm. of substance, heated with a mixture of carbonate and chlorate of potassium, gave 0·8355 grm. of sulphate of barium.

These numbers lead to the formula

$$C_7 H_{15} P S_2 = (C_2 H_5)_3 P + C S_2.$$

	Theory.		Experiment.			
			I.	II.	III.	IV.
C_7	84	43·30	43·43	43·92	43·58	——
H_{15}	15	7·73	7·66	7·67	8·04	——
P	31	15·98	——	——	——	——
S_2	64	32·99	——	——	——	32·72
	194	100·00				

The red crystals are not the only product of the action of disulphide of carbon on triethylphosphine. A second beautifully crystallized compound is deposited after some time from the mother-liquor. This substance, probably a secondary product of the action of the air, is formed in extremely minute quantity; its nature is not yet established.

The compound of triethylphosphine with disulphide of carbon is insoluble in water, sparingly soluble in ether, moderately soluble in disulphide of carbon, and somewhat more soluble in alcohol, especially when heated. The solution has no action on vegetable colours. From the boiling alcoholic solution, it separates on cooling in red needles, somewhat resembling the crystals of chromic acid, which are formed by the action of strong sulphuric acid in a solution of chromate of potassium. The ethereal solution, left to evaporate in an open cylinder, deposits finely developed, deep-red crystals of considerable size. QUINTINO SELLA has examined these crystals with the following results.

"System monoclinic:—

$$100, 101 = 29° 41\tfrac{1}{2}'; \quad 010, 111 = 74° 4'; \quad 101, 001 = 27° 7\tfrac{1}{2}'.$$

Forms observed:—

$$100, 010, 001, 110, \bar{1}01 \quad \text{(Fig. 15)}.$$

Combinations observed:—

$$100, 110, 001, \bar{1}01 \cdot \text{(Fig. 16)}.$$
$$100, 110, 001, \bar{1}01, 010 \quad \text{(Fig. 17)}.$$

Fig. 15.

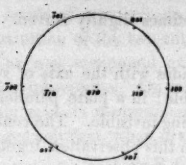


Fig. 16.

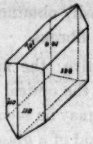
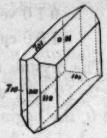


Fig. 17.



Angles.		Calculated.	Observed.
100, 010	=	90° ′	90° 5′
100, 001	=	56 49	56 49
100, 110	=	27 39	27 39
100, $\bar{1}$01	=	114 2	114 2
010, 001	=	90	90 6
010, 110	=	62 21	62 21
010, $\bar{1}$01	=	90	90
001, 110	=	61	60 55
001, $\bar{1}$01	=	57 13	57 13
110, $\bar{1}$01	=	111 9	110 55
110, $\bar{1}$10	=	124 41	124 42

According to NAUMANN:

$$a : b : c = 0{\cdot}9205 : 1 : 1{\cdot}5970; \quad a \circ b = \gamma = 56° 49'.$$

Forms observed:—

$$\infty \breve{P} \infty, \infty \breve{P} \infty, 0P, \infty P, \breve{P} \infty.$$

According to WEISS:—

$$a : b : c = 1 : 1{\cdot}5970 : 0{\cdot}9205; \quad a \circ c = 123° 11'.$$

Forms observed:—

$$a : \infty b : \infty c; \quad \infty a : b : \infty c; \quad \infty a : \infty b : c; \quad a : b : \infty c; \quad -a : \infty b : c.$$

According to LEVY:—

$$M M = 124° 41'; \quad M P = 119°; \quad b : h = 1 : 0{\cdot}4885.$$

Forms observed:—

$$h', g', P, M, a'.$$

The faces are all bright, with the exception of $\bar{1}01$, which is frequently dull, and which, on account of this difference of lustre, may be easily distinguished from 001. The faces 100 and 110 exhibit delicate striæ parallel to the edge of intersection.

Cleavages:—

0 1 0 very distinct and easily obtained, although sometimes slightly curved.
1 0 0 easily obtained and fibrous.

The crystals are optically positive: the medium-line coincides with the axis of symmetry [0 1 0], and the angle of the optical axes is considerable; in a plate parallel to 0 1 0, the beginning of the rings may be seen, their centres being invisible. The centres may be seen, however, with the aid of a glass prism; and from this observation, together with the fact that the indices of refraction are not very far from 1·75, it may be inferred that the interior angle of the optical axes is not very different from 70°. The plane of the optical axes is nearly parallel to the face 0 0 1; it deviates only by a few degrees, exhibiting a tendency to approach the plane perpendicular to 1 0 0. The axis of symmetry, or of smallest elasticity, exhibits a violet-red colour, which even in very thin layers is very intense. The axis nearly parallel to [1 0 0], or the axis of greatest elasticity, exhibits a similar but much lighter red tint; the axis of mean elasticity shows in thin layers a straw-yellow, in thicker layers an orange-yellow. In polarized light one of the most beautiful examples of polychroism is observed by looking across the faces 0 1 0, the colour passing in the case of thin layers from a pure yellow to a deep red. But even in ordinary light the polychroism is perceptible; for the light passes with a violet-red through the faces 1 0 0, and with an orange-red colour of far less intensity through the faces 0 1 0.

Hardness less than that of gypsum."

The red crystals appear to possess the character of a weak base. They dissolve in strong hydrochloric acid, forming a colourless liquid, from which potassa or ammonia throws down the compound in its original state, though somewhat lighter in colour, on account of its minute state of division. The acid solution forms with dichloride of platinum a light yellow amorphous salt, insoluble in alcohol and ether, which changes colour and somewhat decomposes on drying. It darkens in colour, even when dried at the common temperature *in vacuo*, hydrochloric acid fumes being evolved. The analysis of two different preparations gave the following results:—

0·7263 grm. platinum salt, treated with carbonate of sodium, &c., gave 0·1885 grm. =25·95 per cent. of platinum, and 0·7450 grm. of chloride of silver =25·37 per cent. of chlorine.

In a second determination, 0·1900 grm. of platinum-salt, analysed in the same manner, gave 0·200 grm. of chloride of silver =26·04 per cent. of chlorine.

The formula

$$(C_2H_5)_3P,\ CS_2,\ HCl,\ PtCl_2$$

requires 24·66 per cent. of platinum and 26·61 per cent. of chlorine.

The gold-salt is obtained like the platinum-salt, and exhibits similar properties. This salt is not better adapted for analysis.

It is not very easy to form a clear notion of the constitution of the red crystals. According to the formula, the compound is the primary triethylphosphonium-salt of sulphocarbonic acid *minus* 1 equiv. of sulphuretted hydrogen, and corresponds therefore

to sulphocarbamic acid, the ammonium salt of which, as is well known, is produced by the action of ammonia on disulphide of carbon. There is, however, no analogy in the constitution of the two substances.

The new compound exhibits a remarkable tendency to pass into the sulphide of triethylphosphine. On mixing its alcoholic solution with oxide or nitrate of silver, carbonic acid is evolved, sulphide of silver and metallic silver are separated, and the filtered solution, when evaporated, deposits crystals of the sulphide:

$$(C_2H_5)_3P,CS_2+2Ag_2O=Ag_2S+Ag_2+CO_2+(C_2H_5)_3PS.$$

The disulphide-of-carbon-compound undergoes a similar change, even under the influence of moisture. Crystals, not dried with sufficient care, when kept in corked tubes, were changed after a few months into a yellowish white semifluid mass, of peculiar odour, which, by recrystallization from boiling water, furnished a considerable quantity of pure sulphide of triethylphosphine. To establish this transformation by numbers, the purified crystals were identified by analysis.

I. 0·5345 grm. of the sulphide gave 0·9440 grm. of carbonic acid and 0·4915 grm. of water.

II. 0·2460 grm. of the sulphide, oxidized with nitric acid, gave 0·3810 of sulphate of barium.

The formula

$$C_6H_{15}PS=(C_2H_5)_3PS$$

requires—

	Theory.		Experiment.	
			I.	II.
C_6	72	48·00	48·16	——
H_{15}	15	10·00	10·21	——
P	31	20·67	——	——
S	32	21·33	——	21·27
	150	100·00		

It is obvious that the transformation of the red crystals into the sulphide involves the co-operation of the elements of water. Perfectly dry crystals were preserved in sealed tubes for many months without the slightest alteration. The crystals fuse at 95° and volatilize at 100°; in the absence of moisture, they may be heated under pressure to 150° without undergoing any decomposition. The phenomena are very different in the presence of water. When exposed for some days in sealed tubes with water to a temperature of 100°, the red crystals are gradually transformed into white needles, which are easily recognized as sulphide of triethylphosphine. The transformation is independent of atmospheric air; for it takes place with equal facility in vessels filled with air, or carbonic acid, or *in vacuo*.

The products which accompany the sulphide formed in this reaction vary according to the time during which the red crystals are digested with water. If the tubes be allowed to cool after one or two days' digestion, the liquid generally becomes filled with

white needles, which are, however, still intermixed with red prisms, showing that the transformation is not yet complete. Scarcely any gas escapes when the tubes are opened, but when gently heated, the liquid yields abundance of disulphide of carbon. On the other hand, when the tubes are heated until the transformation of the red compound is accomplished,—which generally takes place after three or four days' digestion,—a large volume of gas escapes on opening, and the tubes are occasionally shattered. The gas which is thus evolved consists of sulphuretted hydrogen and carbonic acid, which are obviously secondary products of the reaction, arising from the protracted action of the water upon the disulphide of carbon which is separated in the first stage of the process. The liquid, from which the crystals of the sulphide have been deposited, has a distinctly alkaline reaction, belonging neither to the sulphide nor to the red crystals from which the sulphide arises, both these compounds being without action on vegetable colours. To seize the basic substance, the liquid was evaporated on the water-bath, till the sulphide had been as far as possible expelled, and then precipitated with iodide of zinc, which does not combine with the sulphide, traces of this body, which might have remained, being in this manner eliminated. The iodide-of-zinc-precipitate was semi-solid, and slowly became crystalline on treatment with alcohol; it did not, however, exhibit a sufficiently definite appearance to warrant its analysis. The bases were therefore at once liberated again by digesting the precipitate with oxide of silver; the powerfully alkaline liquid thus obtained gave, on addition of hydrochloric acid and dichloride of platinum, a difficultly soluble platinum-salt, crystallizing, after the necessary purification, from boiling water in splendid octohedra, which on analysis proved to be the methyl-triethylphosphonium-compound.

0·3799 grm. platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1110 grm. =29·21 per cent. of platinum.

The formula

$$[(CH_3)(C_2H_5)_3P]Cl, PtCl_2$$

requires 29·18 per cent. of platinum.

The solution filtered off from the octohedral salt gave, on evaporation, the extremely soluble six-sided tables of the platinum-salt of oxide of triethylphosphine, which I have mentioned in the commencement of this paper.

The products of the action of water upon the red crystals, then, are sulphide of triethylphosphine—the principal product,—oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and disulphide of carbon, which may be partly or entirely converted into sulphuretted hydrogen and carbonic acid. Four molecules of the disulphide-of-carbon-compound and two molecules of water contain the elements of two molecules of the sulphide, one molecule of the oxide, one molecule of the hydrated phosphonium, and three molecules of disulphide of carbon.

$$4[(C_2H_5)_3P, CS_2]+2\left[\begin{matrix}H\\H\end{matrix}\right\}O=2[(C_2H_5)_3PS]+(C_2H_5)_3PO+\left[\begin{matrix}(CH_3)(C_2H_5)_3P\\H\end{matrix}\right\}O+3CS_2.$$

Whilst engaged with the experiments involved in the elucidation of this subject, I

observed occasionally small, well-defined yellow crystals disseminated among the mixture of white and red needles, which are deposited when the digestion-tubes are allowed to cool, before the transformation is terminated. The yellow crystals appeared in greater quantity towards the close of the operation, and were found to be a secondary product formed by the action of the sulphuretted hydrogen, which is generated in the last stage of the process. I have since learnt to prepare the yellow crystals by a simpler and more definite method. This remarkable compound has become the starting-point of a new inquiry, the result of which I reserve for a later communication.

The formation of the red crystals by the union of triethylphosphine and disulphide of carbon takes place so rapidly, and with such facility, that ever since for the first time I observed this phenomenon, I have used the disulphide of carbon as a reagent for the detection of the phosphorus-bases; for trimethylphosphine exhibits a deportment perfectly similar to that of the ethyl-body. The minutest quantities of these bases may thus be readily and safely recognized. The reaction is best observed by pouring the liquid to be examined upon a watch-glass, and allowing the vapour of the disulphide of carbon to flow from an inclined bottle upon the liquid. Immediately the watch-glass is coated with a beautiful net-work of the red crystals. It requires scarcely to be mentioned that the crystals are not formed when the phosphorus-bases are combined with acids. They appear, however, readily on adding to a mixture of their salts and disulphide of carbon, a drop of potash, which liberates the bases.

On the other hand, triethylphosphine may be employed with the greatest advantage as a test for disulphide of carbon. There is, in fact, no test for this substance, which in delicacy could be compared with it. By its aid the presence of the disulphide in the most volatile fractions of coal-tar-benzol is readily proved; even the exceedingly small quantity of disulphide of carbon diffused in the most carefully purified coal-gas may, as I have shown already in another place*, be recognized without any difficulty. When the gas is passed through a bulb-apparatus containing ether to which a few drops of triethylphosphine are added, the liquid soon assumes a reddish tint, which gradually increases in intensity, until, when the ether is evaporated, the interior of the apparatus appears coated with a delicate efflorescence of the red crystals. Scarcely more than half a cubic foot of the present London coal-gas is required for this experiment.

In order to satisfy myself that disulphide of carbon may be employed with safety as a test for the phosphorus-bases, it was necessary to examine the deportment of this compound with the *arsines* and *stibines*. Disulphide of carbon exhibits no reaction with *triethylarsine* and *triethylstibine*. I have left mixtures of these bases with the disulphide in contact for a considerable length of time, both at the common temperature and at 100°, without being able to observe the slightest alteration. I have also satisfied myself that disulphide of carbon, at all events at the common temperature, is without action upon *phosphoretted hydrogen*.

* Quarterly Journal of the Chemical Society, vol. xiii. p. 87.

On examining somewhat minutely into the deportment of triethylphosphine with sulphur-compounds, the organic sulphocyanates could not be left unnoticed. My attention was in the first place fixed by the sulphocyanate of phenyl, which I had just discovered at the time I was engaged in the study of these reactions. I owe to the kindness of Dr. LEIBIUS a very considerable quantity of this somewhat difficultly obtainable sulphocyanate, the full description of which will be found in a paper on phenyl-derivatives shortly to be published. The deportment of this compound with triethylphosphine, however, is here given in connexion with the phosphorus-bases.

Action of Sulphocyanate of Phenyl upon Triethylphosphine.

The reaction between the two substances in the anhydrous state is very violent, and frequently causes the inflammation of the phosphorus-base. The mixture assumes a deep-yellow colour, and on cooling deposits sometimes splendid uranium-yellow needles; often, however, it remains liquid for hours, and even for days, but suddenly solidifies, when touched with a glass rod, into a hard yellow crystalline mass. The new compound is most conveniently prepared by allowing the sulphocyanate to act upon the triethylphosphine in the presence of a considerable volume of ether. The product of the reaction, being difficultly soluble in cold ether, often separates in the crystalline state, more frequently as an oil, which solidifies after some time. In order to ensure perfect purity, it is only necessary to crystallize the compound once or twice from boiling ether.

I. 0·2160 grm. of the yellow crystals, dried *in vacuo* over sulphuric acid, gave 0·4923 grm. of carbonic acid and 0·1585 grm. of water.

II. 0·2242 grm. of crystals of a second preparation gave 0·5110 grm. of carbonic acid and 0·1675 grm. of water.

III. 0·3491 grm. of substance, burnt with carbonate of sodium and oxide of mercury, gave 0·3250 grm. of sulphate of barium*.

These numbers characterize the new body as a combination of one molecule of triethylphosphine with one molecule of sulphocyanate of phenyl:

$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}P+\left.\begin{matrix}CN\\C_6H_5\end{matrix}\right\}S=C_{13}H_{20}NPS.$$

	Theory.		Experiment.		
			I.	II.	III.
C_{13}	156	61·66	62·16	62·16	——
H_{20}	20	7·90	8·14	8·30	——
N	14	5·54	——	——	——
P	31	12·25	——	——	——
S	32	12·65	——	——	12·79
	253	100·00			

* When attempting to determine the sulphur as sulphide of silver, I found that on ebullition of the

The above formula is fully corroborated by the analysis of several well-defined salts, which will be mentioned presently.

The yellow crystals are insoluble in water. Alcohol, both cold and hot, dissolves them in almost every proportion. The best crystals were obtained by the spontaneous evaporation of the ethereal solution in a high open cylinder. Some of these crystals were so well developed, that QUINTINO SELLA was enabled to submit them to a detailed crystallographic examination, which I here insert.

"System monoclinic:—

100, 001=61° 2′; 010, 110=44° 27′.

Forms observed:—

100, 010, 001, 110 (Fig. 18).

Combinations observed:—

110, 001 (Fig. 19).

110, 100, 001 (Fig. 20).

110, 001; 100, 010 (Fig. 21).

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Fig. 18.

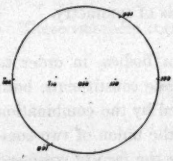


Fig. 19.

Fig. 20.

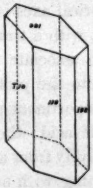
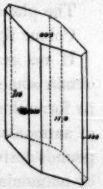


Fig. 21.



Angles.		Calculated.	Observed.
		° ′	° ′
100, 010	=	90 0	90 0
100, 001	=	61 2	60 53
100, 110	=	45 33	45 33
010, 001	=	90 0	——
010, 110	=	44 27	44 27
001, 110	=	70 10	70 24
110, $\bar{1}$10	=	88 54	88 54

alcoholic solution with nitrate of silver not more than about one-half of the sulphur was separated as sulphide of silver. 0·3180 grm. of substance gave 0·1491 grm. of sulphide of silver=6·05 per cent. of sulphur. In the presence of ammonia the whole amount of sulphur is precipitated as sulphide of silver.

According to NAUMANN:—

$$b:c=1:0{\cdot}8583;\quad \gamma=61°\,2'.$$

Forms observed:—

$$\infty P\infty,\ \infty P\!\!\breve{}\infty,\ 0P,\ \infty P.$$

According to WEISS:—

$$a:b=1:0{\cdot}8583;\quad a\,o\,c=118°\,58'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:b:\infty c;\quad \infty a:\infty b:c;\quad a:b:\infty c.$$

According to LEVY:—

$$M\,M=88°\,54';\quad M\,P=109°\,50'.$$

Forms observed:—

$$h',\ g',\ P,\ M.$$

The faces 0 0 1 present less lustre than the others, which are very brilliant, when the crystals are taken from a tube which contains a number of the crystals. In contact with the air they become opaque, and the faces lose their lustre, but they become again transparent when returned to the tube containing the other crystals.

Cleavage 1 0 0 easily obtained; cleavage 1 1 0 fibrous.

Hardness nearly that of gypsum.

The plane of the optical axes is parallel to [0 1 0], or to the axis of symmetry.

Colour light yellow, with a tint of green."

If we endeavour to associate this compound with well-known bodies, in order to obtain some insight into the probable arrangement of its proximate constituents, both its formation and its deportment point to *urea*. Urea is generated by the combination of ammonia and cyanic acid: the yellow crystals are formed by the union of two compounds derived respectively from ammonia and cyanic acid; in urea the faculty possessed by ammonia of combining with acids has been preserved; the new compound likewise exhibits the sharply-defined characters of a monacid base. Whatever constitution be attributed to urea, must also be claimed for the new base. If urea be viewed as a monacid diamine,

$$C\,H_4\,N_2\,O = \left.\begin{matrix}(C\,O)'' \\ H_2 \\ H_2\end{matrix}\right\} N_2,$$

the yellow crystals present themselves as

$$C_{13}\,H_{20}\,N\,P\,S = \left.\begin{matrix}(C\,S)'' \\ (C_2\,H_5)_2 \\ (C_2\,H_5)(C_6\,H_5)\end{matrix}\right\} N\,P.$$

The new compound accordingly belongs to the type urea: it may be viewed as ordinary urea, the oxygen of which is replaced by sulphur, for the hydrogen of which ethyl and phenyl have been substituted, whilst phosphorus has taken the place of half the nitrogen. Regarded from this point of view, the formation of the new compound presents considerable interest; it offers the first example of the perfect substitution of the

hydrogen in urea, which had remained doubtful hitherto, and illustrates in a remarkable manner the persistence of the type urea under the influence of an almost overwhelming substitution. At the same time it deserves to be noticed that the corresponding oxygenated urea remains to be discovered.

The new compound, as already mentioned, possesses the properties of a well-defined organic base. Insoluble in water, it dissolves with the greatest facility even in very diluted acids, giving rise in many cases to easily-crystallizable salts which are capable of double decomposition, and from which the base may be reprecipitated by the careful addition of potassa or ammonia.

Chloride.—The solution of the phenyl-compound in warm concentrated hydrochloric acid solidifies on cooling to a crystalline mass, which, when recrystallized from moderately warm water, furnishes splendid cadmium-yellow crystals, frequently an inch in length. Boiling water has to be avoided, since it decomposes the substance. Even the dry crystals are altered at 100°; they must therefore, like all the other salts of the base, be dried *in vacuo* over sulphuric acid.

I. 0·1953 grm. of substance gave 0·3850 grm. of carbonic acid and 0·1293 grm. of water.

II. 0·5635 grm. of substance gave 0·2850 grm. of chloride of silver.

These numbers correspond to the formula

$$C_{13}H_{21}NPSCl = \left[\begin{matrix}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{matrix}\right\}NP\Big]Cl.$$

	Theory.		Experiment.	
			I.	II.
C_{13}	156	53·88	53·76	——
H_{21}	21	7·25	7·36	——
N	14	4·84	——	——
P	31	10·71	——	——
S	32	11·06	——	——
Cl	35·5	12·26	——	12·51
	289·5	100·00		

Bromide.—Both in preparation and properties, precisely similar to the salt previously mentioned.

0·2835 grm. of bromide gave 0·1620 grm. of bromide of silver.

The formula

$$C_{13}H_{21}NPSBr = \left[\begin{matrix}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{matrix}\right\}NP\Big]Br$$

requires the following values:—

		Theory.	Experiment.
1 equiv. of Phenyl-compound	253	75·76	——
1 equiv. of Hydrogen	1	0·29	——
1 equiv. of Bromine	80	23·95	24·31
1 equiv. of Bromide	334	100·00	

Platinum-salt.—The solution of the chloride furnishes with dichloride of platinum a light-yellow crystalline precipitate. Dilute solutions slowly deposit this salt in somewhat better-formed crystals, which are frequently grouped in lily-shaped aggregations.

0·4690 grm. of platinum-salt, heated with carbonate of sodium, gave 0·0995 grm. of platinum and 0·4505 grm. of chloride of silver.

The formula

$$C_{13}H_{21}NPSPtCl_3 = \left[\begin{matrix}(CS)'' \\ H(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\}NP\left]Cl,\ PtCl_2$$

requires the following values:—

		Theory.	Experiment.
1 equiv. of Phenyl-compound	253	55·11	——
1 equiv. of Hydrogen	1	0·21	——
1 equiv. of Platinum	98·7	21·49	21·22
3 equivs. of Chlorine	106·5	23·19	23·75
1 equiv. of Platinum-salt	459·2	100·00	

I did not succeed in preparing the sulphate or the nitrate of the base. The phenyl-compound is rapidly decomposed under the influence of these acids; it forms, however, beautifully crystallized salts with the iodides of methyl and ethyl. I have examined only the former of these compounds.

Iodide-of-Methyl-compound.—When iodide of methyl is poured into an ethereal solution of the urea, the new compound is at once separated as a heavy oil which rapidly solidifies into a crystalline mass. The crystals dissolve in boiling water which on cooling deposits the iodide in splendid needles of a golden-yellow colour.

These crystals contain

$$C_{14}H_{23}NPSI = \left[\begin{matrix}(CS)'' \\ CH_3(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\}NP\left]I.$$

0·3885 grm. of iodide gave 0·2300 grm. of iodide of silver.

		Theory.	Experiment.
1 equiv. of Phenyl-compound	253	64·06	——
1 equiv. of Methyl	15	3·79	——
1 equiv. of Iodine	127	32·15	31·97
1 equiv. of Iodide	395	100·00	

Platinum-salt of the Methyl-compound.

The chloride obtained by treating the iodide with chloride of silver, yields upon addition of dichloride of platinum, an acicular platinum-salt, which may be recrystallized without decomposition from boiling water. Its composition corresponds to that of the iodide:

$$C_{14}H_{23}NPSPtCl_3 = \left[\begin{matrix}(CS)''\\(CH_3)(C_2H_5)_2\\(C_2H_5)(C_6H_5)\end{matrix}\right\}NP\left]Cl,\ PtCl_2.\right.$$

0·3395 grm. of platinum-salt, treated with carbonate of sodium, gave 0·0700 grm. of platinum and 0·3095 grm. of chloride of silver.

	Theory.		Experiment.
1 equiv. of Phenyl-compound .	253	53·47	——
1 equiv. of Methyl	15	3·16	——
1 equiv. of Platinum . . .	98·7	20·86	20·62
3 equivs. of Chlorine . . .	106·5	22·51	22·55
1 equiv. of Platinum-salt . .	473·2	100·00	

The iodide, when treated with oxide of silver, furnishes, together with iodide of silver, a very caustic liquid containing the corresponding hydrate. The presence in this liquid of the compound

$$C_{14}H_{24}NPSO = \left.\begin{matrix}[(CH_3)\{(CS)''(C_2H_5)_3(C_6H_5)NP]\\H\end{matrix}\right\}O,$$

is proved by the fact of the characteristic needle-shaped platinum-salt being immediately reproduced when it is saturated with hydrochloric acid and mixed with dichloride of platinum. The free base is, however, readily decomposed. On boiling, the odour of sulphocyanate of phenyl becomes at once perceptible; if ebullition be continued until the odour has disappeared, addition of hydrochloric acid and dichloride of platinum no longer furnishes the difficultly soluble needles. In their place, large well-developed orange-yellow octohedra are deposited on evaporation, which by analysis were found to be the platinum-salt of methyl-triethylphosphonium.

0·2210 grm. of platinum-salt, precipitated by sulphuretted hydrogen, &c., gave 0·0640 grm. = 28·96 per cent. of platinum.

The formula

$$[(CH_3)(C_2H_5)_3P]Cl,\ PtCl_2$$

requires 29·18 per cent. of platinum.

The free methylated phenyl-base then simply splits by ebullition into sulphocyanate of phenyl and oxide of methyl-triethylphosphonium. When the solution is boiled by itself, the sulphocyanate is separated as such; when it is boiled in the presence of oxide of silver, the sulphocyanate is, partly at least, destroyed, the alkaline solution becoming acid and exhibiting the presence of considerable quantities of sulphuric acid. This transformation clearly shows how feebly the proximate constituents are held together

in the urea. The same instability is perceptible in the general deportment of the compound. Even extremely dilute nitric acid liberates the sulphocyanate of phenyl, whilst the phosphorus-base is converted into the oxide. The chloride is one of the more stable salts of the urea, but it is likewise readily altered; on addition of a large quantity of water, the solution of the salt becomes milky, the sulphocyanate of phenyl being separated in oily globules, and now contains the chloride of triethylphosphonium. On adding ammonia to the *concentrated* solution of the chloride, the urea, as has been already stated, is separated without change, and may be readily recovered by taking up with ether and crystallizing. If, on the other hand, the *dilute* solution be boiled with ammonia, the turbidity perceptible in the commencement disappears again, and after a few moments beautiful crystals of *phenyl-sulphocarbamide* are deposited, triethylphosphine being simultaneously liberated:

$$\left.\begin{matrix}(CS)''\\(C_2H_5)_3\\(C_6H_5)\end{matrix}\right\}NP + H_3N = (C_2H_5)_3P + \left.\begin{matrix}(CS)''\\(C_6H_5)\\H_3\end{matrix}\right\}N_2.$$

On treating the chloride with potassa, phenomena exactly analogous are observed; the crystals which are separated, are, however, *diphenyl-sulphocarbamide*:

$$2\left[\left.\begin{matrix}(CS)''\\(C_2H_5)_3\\(C_6H_5)\end{matrix}\right\}NP\right] + 4\left[\left.\begin{matrix}K\\H\end{matrix}\right\}O\right] = \left.\begin{matrix}K\\K\end{matrix}\right\}S + \left.\begin{matrix}K\\K\end{matrix}\right\}CO_3 + \left.\begin{matrix}H\\H\end{matrix}\right\}O + 2[(C_2H_5)_3P] + \left.\begin{matrix}(CS)''\\(C_6H_5)_2\\H_2\end{matrix}\right\}N_2.$$

If a few drops of disulphide of carbon be added to the solution of the urea, the liquid, when gently heated, assumes a deep red colour, and deposits on cooling the beautiful ruby-red crystals $(C_2H_5)_3P, CS_2$, which I have mentioned in a previous paragraph of this paper. The mother-liquor of these crystals furnishes on evaporation oily droplets of sulphocyanate of phenyl. The urea, even when perfectly pure and dry, cannot be preserved without undergoing a gradual alteration. If the crystals be left under a bell-jar containing atmospheric air, they become dull, and at last moist and sticky, whilst a peculiar extremely disagreeable odour, distantly resembling that of hydrocyanic acid, becomes perceptible; at the same time, a delicate net-work of fine needles begins to appear on the glass, easily recognized as sulphide of triethylphosphine. The crystals of the urea fuse at 57°·5, forming a yellow liquid, which, in consequence of incipient decomposition, resolidifies but slowly and imperfectly. At 100° the phenomena just mentioned are much more distinctly observed, and especially the smelling body is unmistakeably perceived. The peculiar-smelling body is likewise almost overwhelmingly produced on evaporating the ethereal mother-liquor of the compound. As yet I have not been able to lay hold of the possessor of this remarkable odour. The ethereal mother-liquor, when evaporated, leaves a brown syrup, which after some time deposits large crystals of sulphide of triethylphosphine. Submitted to distillation, this residue yields, together with other products, an additional quantity of the crystallized sulphur-compound.

Transformations precisely similar are observed when the crystals of the urea, in sealed tubes, are exposed to a temperature of from 150° to 160°. The brown fused mass which is thus formed, solidifies on cooling with crystalline structure; the crystals, however, are no longer the original compound, but sulphide of triethylphosphine, which is surrounded by another substance. The examination of this reaction has not yet been completed. The nature of the final products of the metamorphosis may, however, be anticipated in some measure by the results obtained in studying the deportment of triethylphosphine with *sulphocyanate of ethyl* and *sulphocyanate of ethylene*, which will be briefly mentioned in some of the following paragraphs.

Action of Sulphocyanate of Allyl upon Triethylphosphine.

To generalize the relations established in the preceding paragraph, I was induced to examine the deportment of the phosphorus-base with oil of mustard. The two bodies act upon each other with extraordinary violence; the mixture turns brown, but does not solidify either by cooling or by agitation. After some days, however, the syrup yields brown crystals which are difficult to purify. The purification of the compound succeeds, however, without any difficulty when the reaction is allowed to take place in ether. In this manner a crystalline mass is easily obtained, which requires only to be washed with cold ether, and then once recrystallized from boiling ether.

0·3623 grm. of the substance, dried over sulphuric acid *in vacuo*, gave 0·7368 grm. of carbonic acid and 0·3040 grm. of water.

The formula

$$C_{10}H_{20}NPS = \left.\begin{matrix}(CS)'' \\ (C_2H_5)_2 \\ (C_2H_5)(C_3H_5)\end{matrix}\right\}NP$$

requires the following values:—

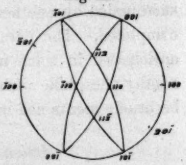
		Theory.	Experiment.
C_{10}	120	55·30	55·46
H_{20}	20	9·21	9·32
N	14	6·45	——
P	31	14·29	——
S	32	14·75	——
	217	100·00	

The allyl-compound behaves in all respects like the phenyl-compound. It is insoluble in water, but easily soluble in alcohol; the solution has a faintly alkaline reaction. It fuses at 68° and solidifies at 61°. At a higher temperature, it is decomposed exactly like the phenyl-compound. In this case also, a peculiar, and if possible, still more repulsive odour is evolved, while crystals of sulphide of triethylphosphine separate in large quantity.

The allyl-compound crystallizes with extraordinary facility. There is no difficulty in obtaining it in colourless transparent crystals half an inch in length, and perfectly deve-

loped on all sides. I scarcely remember any other organic compound that crystallizes so readily. The crystals, as appears from the measurements of QUINTINO SELLA, are isomorphous with those of the corresponding phenyl-compound*. SELLA has communicated to me the following details respecting his examination.

Fig. 22.



"System monoclinic:—

100, 101=35° 42′; 001, 101=29° 3′; 010, 111=39° 22′.

Forms observed:—

100, 001, 110, $\bar{1}01$, $\bar{2}01$, $\bar{1}12$ (Fig. 22).

Angles.		Calculated.	Observed.
100, 001	=	64° 45′	64° 45′
100, 110	=	66 14	66 14
100, $\bar{1}01$	=	114 9	114 9
100, $\bar{2}01$	=	143 51	143 54
100, $\bar{1}12$	=	89 32	89 13
001, 110	=	80 15	80 10
001, $\bar{1}01$	=	49 24	49 25
001, $\bar{2}01$	=	79 6	79 7
001, $\bar{1}12$	=	51 8	51 17
110, $\bar{1}10$	=	47 33	47 31
110, $\bar{1}01$	=	99 30	99 30
110, $\bar{2}01$	=	109 0	108 54
110, $\bar{1}12$	=	48 23	48 41
110, $11\bar{2}$	=	48 37	48 34
$\bar{1}01$, $\bar{2}01$	=	29 41	29 38
$\bar{1}01$, $\bar{1}12$	=	51 7	51 2
$\bar{2}01$, $\bar{1}12$	=	66 20	67 5
$\bar{1}12$, $11\bar{2}$	=	87 31	87 55

According to NAUMANN:—

$a:b:c=0{\cdot}8321:1:0{\cdot}3984$; $\gamma=64°\ 45′$.

Forms observed:—

$\infty P\infty$; $0P$, ∞P, $P\infty$, $2P\infty$, $\frac{1}{2}P$.

* Both substances are isomorphous with thiosinamine or sulphallyl-ures,

$$\left.\begin{matrix}(CS)''\\(C_3H_5)H\\H_2\end{matrix}\right\}N_2,$$

the crystalline form of which has been determined by SCHABUS.

According to Weiss:—

$$a:b:c=1:0{\cdot}3984:0{\cdot}8321;\quad a\,o\,c=115°\,15'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:\infty b:c;\quad a:b:\infty c;\quad -a:\infty b:c;\quad -\tfrac{1}{2}a:\infty b:c;\quad -a:b:\tfrac{1}{2}c.$$

According to Levy:—

$$\mathrm{M\,M}=47°\,33';\quad \mathrm{M\,P}=99°\,45';\quad b:h=1:0{\cdot}7730.$$

Forms observed:—

$$h',\ \mathrm{P},\ \mathrm{M},\ a',\ a^{\frac{1}{2}},\ b'.$$

Combinations observed:—

0 0 1, 1 0 0, 1 1 0 (Fig. 23).

0 0 1, $\bar{1}$ 0 1, 1 1 0 (Fig. 24).

1 0 0, 0 0 1, $\bar{1}$ 0 1, 1 1 0 (Fig. 25).

1 0 0, 0 0 1, $\bar{1}$ 0 1, 1 1 0; $\bar{1}$ 1 2 (Fig. 26).

1 0 0, 0 0 1, $\bar{1}$ 0 1, 1 1 0, $\bar{2}$ 0 1, $\bar{1}$ 1 2 (Fig. 27).

Fig. 23.

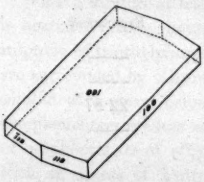


Fig. 24.

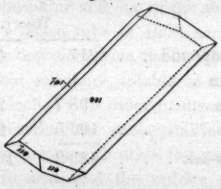
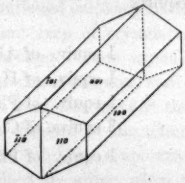


Fig. 25.



The crystals sometimes present the appearance of trimetric crystals (Fig. 25), sometimes they are flattened parallel with 0 0 1, and considerably elongated in the direction [0 1 0] (Figs. 23, 24). The faces $\bar{1}$ 1 2 are rounded off and cannot be well measured, although it is possible to verify the zones to which they belong: some of these faces are occasionally wanting, and many of the crystals present only two of these faces (Fig. 27).

Cleavages 1 0 0 and 0 0 1 distinct, and easily obtained.

Fig. 26.

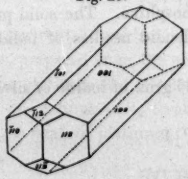
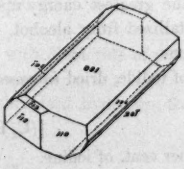


Fig. 27.



The optical axes are situated in the plane of symmetry, viz. 0 1 0. The bisecting line is not very far from normal to $\bar{1}$ 0 1. A system of rings is observed both through the

faces 1 0 0 and through the faces 2 0 $\bar{1}$; another system is seen through the faces 0 0 1. The apparent angle of the optical axes is about 38°, if the first system of rings be observed through 1 0 0, and about 68½° if this system be seen through 2 0 $\bar{1}$. The mean index of refraction, *i. e.* of that which corresponds to a ray lying in a plane parallel to 0 1 0 and polarized in that plane, is $\beta = 1{\cdot}657$. Hence it follows that the internal angle of the optical axes is about 72½°.

Hardness less than that of gypsum."

Platinum-salt.—I have contented myself with verifying the formula of the allyl-urea by the analysis of the platinum-salt. The allyl-compound dissolves readily in hydrochloric acid, and the solution, when mixed with dichloride of platinum, yields a light-yellow scaly precipitate having a silky lustre, which fuses to a yellow oil in boiling water.

0·5605 grm. of the crystals, dried over sulphuric acid, precipitated by sulphuretted hydrogen, &c., gave 0·1282 grm. of platinum.

The formula

$$C_{10}H_{21}NPSPtCl_3 = \left[\begin{matrix}(C\,S)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_3H_5)\end{matrix}\right\}NP\left.\right]Cl,\,PtCl_2$$

requires

	Theory.		Experiment.
1 equiv. of Allyl-compound . .	217	51·28	——
1 equiv. of Hydrogen	1	0·23	——
1 equiv. of Platinum	98·7	23·32	22·87
3 equivs. of Chlorine	106·5	25·17	——
1 equiv. of Platinum-salt . . .	423·2	100·00	

The allyl-base described in the preceding pages has the composition of sulphocyanate of triethyl-allylphosphonium:

$$\left.\begin{matrix}(C\,S)''\\ (C_2H_5)_2\\ (C_2H_5)(C_3H_5)\end{matrix}\right\}NP = \left.\begin{matrix}CN\\ [(C_2H_5)_3(C_3H_5)\,P]\end{matrix}\right\}S.$$

I felt some interest in comparing the latter compound with the allyl-base. Iodide of allyl acts with the greatest energy upon triethylphosphine. The solid product of the reaction, recrystallized from alcohol, furnishes splendid needles of iodide of triethyl-allylphosphonium.

0·6740 grm. of iodide, dried *in vacuo*, gave 0·5535 grm. of iodide of silver = 44·38 per cent. of iodine.

The formula $[(C_2H_5)_3(C_3H_5)\,P]I$

requires 44·40 per cent. of iodine.

Treatment with chloride and oxide of silver yields the corresponding chloride and hydrate. They resemble in every respect the tetrethylphosphonium-compounds. The

chloride gives with dichloride of platinum an easily crystallizable octohedral platinum-salt.

The hydrate of triethyl-allylphosphonium forms with hydrosulphocyanic acid a difficultly crystallizable salt which is easily soluble in water, and differs, as might have been expected, entirely from the allyl-base, which has the same composition.

Behaviour of Triethylphosphine with the Sulphocyanates of Ethyl and Ethylene.

I have in vain endeavoured to produce, by the action of triethylphosphine on the sulphocyanates of methyl, ethyl, and amyl, compound ureas analogous to the allyl- and phenyl-bodies. It is true that these substances act upon triethylphosphine even at ordinary temperatures; in the case of sulphocyanate of methyl, indeed, the action is very brisk, but I did not succeed in obtaining definite compounds. Sulphocyanate of ethyl remained for months in contact with triethylphosphine without depositing any crystalline compound. The non-production of these ureas cannot, however, excite surprise, if we remember in how many respects, and especially in their relation to ammonia, the sulphocyanogen-compounds of ethyl and its homologues differ from those of allyl and phenyl.

When a mixture of triethylphosphine and one of the above-mentioned sulphocyanates is heated for some hours in a sealed tube to 100°, an abundant crop of crystals of sulphide of triethylphosphine is deposited from the liquid after cooling. These crystals are surrounded by a brown viscid substance, soluble to a certain extent in water, easily soluble with green colour in alcohol. In order to disentangle from this mixture the complementary product of the reaction, the semicrystalline mass, obtained by the action of sulphocyanate of ethyl, was shaken with ether to separate the sulphide, evaporated with an excess of hydrochloric acid, and the residue redissolved in water, when a quantity of the brown impurities remained insoluble. The filtered solution gave with trichloride of gold a dingy yellow precipitate, which by treatment with sulphuretted hydrogen, reprecipitation of the separated chloride by trichloride of gold, &c., ultimately assumed the characters of the pure gold-salt of *tetrethylphosphonium*.

0·2240 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0·0910 grm. =40·62 per cent. of gold.

The formula

$$[(C_2H_5)_4P]Cl,\ AuCl_3$$

requires 40·53 per cent. of gold.

The chloride, prepared from the gold-salt, gave with dichloride of platinum beautiful octohedra of the platinum-salt of tetrethylphosphonium.

0·6300 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1784 grm. =28·31 per. cent. of platinum.

The formula

$$[(C_2H_5)_4P]Cl,\ PtCl_2$$

requires 28·02 per cent. of platinum.

The action of sulphocyanate of ethyl upon triethylphosphine may be accordingly

represented by the equation

$$\left.\begin{matrix} C\,N \\ C_2H_5 \end{matrix}\right\}S + 2\left[(C_2H_5)_3P\right] + \left.\begin{matrix} H \\ H \end{matrix}\right\}O = (C_2H_5)_3PS + \left.\begin{matrix} \left[(C_2H_5)_4P\right] \\ H \end{matrix}\right\}O + HCN.$$

I have not been able to trace directly the hydrocyanic acid which figures in this equation, but this acid appears unmistakeably in its products of decomposition. The brown substance which accompanies the sulphide of triethylphosphine and the hydrate of tetrethylphosphonium is rich in nitrogen; boiled for some time with hydrochloric acid, it yields abundance of chloride of ammonium. In fact, it was on account of the presence of ammonia among the products of the reaction, that it became necessary to precipitate the tetrethylphosphonium in the first place in the form of the gold-compound.

I have likewise examined the behaviour of disulphocyanate of ethylene with triethylphosphine. The reaction takes place with energy at ordinary temperatures. When triethylphosphine is poured into a concentrated alcoholic solution of sulphocyanate of ethylene, the liquid immediately solidifies to a dazzling white crystalline mass of sulphide of triethylphosphine. It deserves to be noticed that the same decomposition takes place also when the substances are allowed to react in the presence of anhydrous ether. The transformation which the sulphocyanate of ethylene undergoes under the influence of triethylphosphine is perfectly analogous to the change of the ethyl-compound when submitted to the same agent. Instead of a derivative of tetrethylphosphonium, the sulphocyanate of ethylene produces the cyanide of a diatomic metal, of *ethylene-hexethyl-diphosphonium*.

$$\underbrace{\left.\begin{matrix} (CN)_2 \\ (C_2H_4)'' \end{matrix}\right\}S_2}_{\text{Sulphocyanate of ethylene.}} + 4\underbrace{\left[(C_2H_5)_3P\right]}_{\text{Triethylphosphine.}} = 2\underbrace{\left[(C_2H_5)_3PS\right]}_{\text{Sulphide of triethylphosphine.}} + \underbrace{\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3P\end{matrix}\right]''(CN)_2}_{\text{Dicyanide of ethylene-hexethyl-diphosphonium.}}.$$

Owing to the low temperature at which the reaction is accomplished, the hydrocyanic acid is not changed in this case, and may be recognized without difficulty by the ordinary reagents. The diphosphonium, which is simultaneously formed, was traced as platinum-salt, exactly in the same manner as the tetrethylphosphonium in the process previously mentioned. The product of the reaction, freed as far as possible from the sulphide by repeated evaporation and ultimately by treatment with ether, was precipitated by dichloride of platinum. The dingy platinum-salt was purified by treatment with sulphuretted hydrogen and reprecipitation. Repeatedly treated in this manner, it assumed the character of a pure compound.

0·2745 grm. of this salt gave 0·0804 grm. =29·29 per cent. of platinum.

The formula

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3P\end{matrix}\right]''Cl_2, 2PtCl_2$$

requires 29·27 per cent. of platinum. Since I shall have to give a detailed account of

the diphosphonium-compounds in one of the following sections of this inquiry, I need not for the present enter into further particulars regarding this reaction.

In concluding this paragraph, I may append a few remarks upon the deportment of sulphocyanate of triethylphosphonium under the influence of heat. This salt is readily procured by dissolving triethylphosphine in hydrosulphocyanic acid. Submitted to the action of heat, it is partly volatilized without decomposition; the greater portion, however, is decomposed, the sulphide and the disulphide-of-carbon-compound of triethylphosphine, together with free disulphide of carbon, appearing among the volatile products of the reaction; while a brown ill-defined substance remains in the retort, yielding, when treated with an alkali, an appreciable quantity of ammonia. I have not examined this change in detail, but it is obvious that one of the direct products of the reaction is sulphocyanate of ammonium, the further decomposition of which explains the appearance of the disulphide of carbon, as well as the other products observed. The residue, of course, must contain the varied compounds generated by the action of heat on sulphocyanate of ammonium.

Behaviour of the Arsines and Stibines with the Sulphocyanates of Phenyl and Allyl.

The facility with which the compound ureas containing nitrogen and phosphorus are formed, induced me to attempt the production of analogous compounds with arsenic or antimony in place of phosphorus. I therefore treated sulphocyanate of phenyl and oil of mustard successively with triethylarsine and triethylstibine, first at ordinary and then at gradually increasing temperatures in sealed tubes. But not one of these experiments led to the expected result. The arsines and stibines differ, indeed, in their chemical characters much more from ammonia than the phosphines. Their incapability of forming saline compounds with acids is alone sufficient to render the formation of ureas containing arsenic and antimony somewhat improbable. When mixtures of triethylarsine with sulphocyanate of phenyl on the one hand, and sulphocyanate of allyl on the other, were left to stand for some time at ordinary temperatures, the liquid in both cases was found to be traversed by a small quantity of beautiful needle-shaped crystals. The crystals from both mixtures were found to be the same; they were readily identified with the white needles which are gradually formed in triethylarsine when left in contact with atmospheric air.

Behaviour of Triethylphosphine with Cyanates.

The formation of sulphuretted ureas containing phosphorus and nitrogen led me to try whether the corresponding oxygen-compounds could likewise be produced.

When *cyanate of phenyl* is mixed with the phosphorus-base, great heat is evolved, indicating a marked chemical reaction. The mixture on cooling solidifies into a mass of shining crystals which are insoluble in water, nearly insoluble in ether, and dissolve with difficulty even in boiling alcohol. By recrystallization from the last-mentioned solvent, the new body is easily obtained pure. The further examination of the resulting

crystals proved, however, that they by no means consisted of the compound urea of which I was in search. From the analysis, which I intend to give in connexion with other researches, it appeared that the crystals still possessed the composition of cyanate of phenyl, that, indeed, they were *cyanurate of phenyl*. The triethylphosphine in this case appears to induce nothing more than a new molecular disposition of the elements in cyanate of phenyl. The peculiar character of this metamorphosis may be perceived in the most beautiful manner by dipping a glass rod moistened with triethylphosphine into a considerable quantity of cyanate of phenyl. The liquid immediately becomes hot, and solidifies after a few seconds into a shining crystalline mass of the cyanurate.

Similar results were obtained by the action of the phosphorus-base on *cyanate of ethyl*. The two bodies may be mixed without evolution of heat, and the mixture does not solidify; but the transformation is soon indicated by the diminution of the penetrating odour of the cyanate. If, as soon as the odour has disappeared, the liquid be mixed with dilute hydrochloric acid which removes the free phosphorus-base, the oil which floats on the surface quickly solidifies into a solid crystalline mass exhibiting, when recrystallized from boiling water, all the properties of *cyanurate of ethyl*.—When a stream of *cyanic acid* gas is passed through triethylphosphine, the odour of the acid disappears, while the phosphorus-base becomes turbid, and yields a white deposit of *cyanuric acid*.

In connexion with these experiments, I have had occasion to convince myself that *cyanic acid* gas and *phosphoretted hydrogen* do not act upon one another, at least at ordinary temperatures.—I was naturally anxious to ascertain whether the peculiar action of the phosphorus-base on the cyanates extended likewise to the cyanides. I found, however, that *cyanide of methyl* (acetonitrile) or *cyanide of phenyl* (benzonitrile) may be left for days in contact with the phosphorus-base at temperatures varying from 100° to 150°, without experiencing the slightest alteration. Had these substances been changed under the above conditions, like the cyanates, their transformation into methyl- and phenyl-compounds corresponding to cyanethine might have been expected.

Experiments in the Methyl-series.

The information which I have collected with reference to the phosphorus-compounds, has been almost exclusively obtained by the study of triethylphosphine. In exceptional cases only have I worked in the methyl-series. Trimethylphosphine, on account of its volatility, is much less easily prepared than the ethyl-compound, and especially much more difficult to preserve. This body is oxidized with such rapidity, that it disappears from the hands of the operator during manipulation. Its odour, moreover, is insupportable for any length of time.

Nevertheless, I have made a few experiments with the methyl-compound, a slight sketch of which may form the conclusion of this paper.

The phosphorus-derivatives of the methyl-series exhibit the most perfect analogy with the corresponding ethyl-compounds.

Oxide of trimethylphosphine produces with iodide of zinc, with dichloride of platinum, and with trichloride of gold, the homologues of the several compounds obtained from oxide of triethylphosphine.

When trimethylphosphine, either pure or dissolved in alcohol and ether, is submitted to the action of disulphide of carbon, all the phenomena are reproduced which I have mentioned at some length in describing the corresponding ethyl-base. The red crystals which are formed are somewhat paler, much more volatile, and much more readily altered. The disulphide-of-carbon-compounds of the methyl- and ethyl-series exhibit in their properties the same relation which obtains between the sulphides of the two series.

0·2586 grm. of the disulphide-of-carbon-compound gave 0·3030 grm. of carbonic acid and 0·1415 grm. of water.

The formula

$$C_4H_9PS_2 = (CH_3)_3P, CS_2$$

requires the following values:—

	Theory.		Experiment.
C_4	48	31·58	31·95
H_9	9	5·92	6·08
P	31	20·39	——
S_2	64	42·11	——
	152	100·00	

The red crystals are changed with the utmost facility into sulphide of trimethylphosphine. In the hope of forming fine crystals, similar to those obtained with the ethyl-compound, a solution of the red crystals in warm ether was allowed to cool in a tall open cylinder. When the solution was examined next morning it had become colourless, leaving, upon spontaneous evaporation, the beautiful crystals of the sulphur-compound.

The sulphocyanates of phenyl and allyl readily combine with trimethylphosphine. The reaction is even more powerful than with the ethyl-base. The urea-body which trimethylphosphine produces with sulphocyanate of phenyl is a liquid which I have not been able to obtain in the solid state. Directly prepared from the constituents, or separated from one of its crystalline salts, it forms a slightly coloured oily liquid, soluble in water, difficultly soluble in ether, readily soluble in alcohol. On adding concentrated hydrochloric acid to the oil, it gradually solidifies to a crystalline mass of sulphur-yellow delicate, hair-like needles, which may be recrystallized both from water and from alcohol. I have fixed the composition of this phosphoretted urea by a chlorine-determination in the chloride.

0·2718 grm. gave 0·1540 grm. chloride of silver.

The formula

$$C_{10}H_{15}NPSCl = \left[\begin{matrix}(CS)'' \\ H(CH_3)_2 \\ (CH_3)(C_6H_5)\end{matrix}\right\}NP\left]Cl\right.$$

requires

	Theory.		Experiment.
1 equiv. of Urea-compound . . .	211	85·25	——
1 equiv. of Hydrogen	1	0·41	——
1 equiv. of Chlorine	35·5	14·34	14·02
1 equiv. of Chloride	247·5	100·00	

The brown liquid which is formed, with considerable evolution of heat, when trimethylphosphine is brought in contact with mustard oil, gradually deposits well-formed transparent colourless prisms, the habitus of which resembles that of the corresponding ethyl-compound. The crystals were not analysed, but there can be no doubt that they were the methylated phosphorus-urea of the allyl-series

$$C_7H_{14}NPS = \left.\begin{matrix}(CS)'' \\ (CH_3)_2 \\ (CH_3)(C_3H_5)\end{matrix}\right\} NP.$$

Phosphoretted hydrogen is without action on the sulphocyanates of phenyl and allyl.

In conclusion, I beg to thank Drs. A. Leibius and M. Holzmann for their assistance in some of the experiments connected with this inquiry.

XXIII. *Contributions to the History of the Phosphorus-Bases.*

By AUGUSTUS WILLIAM HOFMANN, *F.R.S.*

Received June 21,—Read June 21, 1860.

SECOND MEMOIR.

THEORY OF DIATOMIC BASES.—DIPHOSPHONIUM-COMPOUNDS.

IN surveying the rich harvest of discoveries which of late years have rewarded the exertions of chemists, with reference to their general effect on the progress of the science, we cannot avoid recognizing as one of the most valuable amongst their acquisitions, the development of the theory of polyatomic compounds. Seldom has a theory diffused a clearer light on previously established facts, or exerted a more fructifying and inspiring influence on the labours of chemists. First coming into notice in the classical researches of GRAHAM and LIEBIG on the polybasic acids, and afterwards extended and generalized by the experiments of GERHARDT and WILLIAMSON, it has acquired in BERTHELOT's beautiful investigation of Glycerin, a new field of discovery, the active cultivation of which has already brought to maturity a great variety of fruits. An important step in the development of these ideas was made by H. L. BUFF, in showing that dibromide of ethylene can be converted into a corresponding sulphocyanate, and in the conclusions which he drew from this observation, until, in the brilliant experimental researches of WURTZ on the diatomic alcohols, the doctrine of polyatomic compounds has received its clearest and most elegant expression.

Considering the untiring activity with which chemists have devoted themselves to the study of the polybasic acids and, within the last few years, of the polyatomic alcohols, it cannot but appear remarkable that so little attention should hitherto have been bestowed on the polyacid bases. It is true that we are already in possession of many valuable observations relating to these bodies; but they are isolated, and the facts which they have established can scarcely be looked upon as more than accidental acquisitions. Regarded in the scientific sense as a class, and in their relations to other groups of bodies, the polyatomic bases have hitherto been left without examination.

Respecting the constitution of these compounds, and the conditions under which they would be produced, no doubt could be entertained. For, as from a single molecule of water, a monatomic alcohol, a monobasic acid, or a monacid base can be produced, according to the nature of the monatomic radical by which the hydrogen is replaced, so likewise must it be possible, by a proper selection of polyatomic radicals, to link two or more molecules of water, so as to form one molecule of a polyacid base, just as the introduction of other polyatomic radicals gives rise to the formation of polyatomic alcohols or polybasic acids. It remained only to submit these ideas to the test of experiment.

Material for building up this group of bodies appeared to present itself unmistakeably in the chlorine-, bromine-, and iodine-compounds of ethylene and its homologues. As some years ago I had succeeded in converting the corresponding ethyl-compounds by the action of ammonia into the monacid ethyl-bases, I was justified in expecting that, by treating the ethylene-compounds with ammonia, diacid bases might be formed. Respecting some of the bodies which are produced in these reactions, investigations had already been published by Cloëz*, and more recently by Natanson†, whose results appeared at first sight to give but little encouragement to any such attempt. But a careful examination of these researches soon convinced me that, when viewed by the light which the progress of science has since thrown upon this subject, the results elicited are far from unfavourable to my theoretical conceptions.

I have once more studied these reactions, and have obtained experimental confirmation of the correctness of my anticipations. But the action of ammonia on the chloride, bromide, and iodide of ethylene presents unexpected complications, quite independent of those indicated by theory, and for which I was not altogether prepared.

Consider for a moment the manner in which the reaction between ammonia and a diatomic bromide—dibromide of ethylene for instance—may take place. Just as bromide of ethyl, acting, as it does, on a single molecule of ammonia, gives rise to the formation of the four bromides,

$$[(C_2H_5)\ H_3\,N]\,Br‡,$$
$$[(C_2H_5)_2\,H_2\,N]\,Br,$$
$$[(C_2H_5)_3\,H\ \ N]\,Br,$$
$$\text{and } [(C_2H_5)_4\ \ \ N]\,Br,$$

so likewise may dibromide of ethylene, acting on two molecules of ammonia, be expected to produce four diatomic bromides, viz.—

$$[(C_2H_4)''\,H_6\,N_2]''\,Br_2,$$
$$[(C_2H_4)''_2\,H_4\,N_2]''\,Br_2,$$
$$[(C_2H_4)''_3\,H_2\,N_2]''\,Br_2,$$
$$\text{and } [(C_2H_4)''_4\ \ \ N_2]''\,Br_2.$$

These, however, are by no means the only compounds which, in accordance with our present conception of diatomic compounds, may be formed in this reaction.

It appears from the researches of Wurtz, that dibromide of ethylene does not pass into ethylene-alcohol at a single bound, but that there exists an intermediate member of the series still containing half the bromine,

$$\underbrace{(C_2H_4)''\begin{cases}Br\\Br\end{cases}}_{\text{Dibromide of Ethylene.}} \qquad \underbrace{(C_2H_4)''\begin{cases}Br\\HO\end{cases}}_{\text{Intermediate Bromide.}} \qquad \underbrace{(C_2H_4)''\begin{cases}HO\\HO.\end{cases}}_{\text{Ethylene-alcohol.}}$$

* Instit. 1853, p. 213.

† Ann. Chem. Pharm. xcii. 48. and xcviii. 291.

‡ H=1; O=16; S=32; C=12, &c.

There could, therefore, be no doubt that dibromide of ethylene would, under certain conditions, likewise react with ammonia as a monatomic compound, giving rise to another series of bodies in which the hydrogen would be more or less replaced by the monatomic radical C_2H_4Br, viz.—

$$[(C_2H_4Br)\ H_3N]Br,$$
$$[(C_2H_4Br)_2H_2N]Br,$$
$$[(C_2H_4Br)_3H\ N]Br,$$
$$\text{and } [(C_2H_4Br)_4\quad N]Br.$$

Further, if the reaction took place in presence of water, it was to be expected that the bromine, wholly or partially eliminated as hydrobromic acid, would be replaced by the molecular residue of the water; and thus, independently of any mixed compounds containing bromine *and* oxygen, a series of salts might be looked for, in which a molecule $C_2H_4HO = C_2H_5O$ would enter monatomically, viz.—

$$[(C_2H_5O)\ H_3N]Br,$$
$$[(C_2H_5O)_2H_2N]Br,$$
$$[(C_2H_5O)_3H\ N]Br,$$
$$\text{and } [(C_2H_5O)_4\quad N]Br.$$

Lastly, remembering the tendency exhibited by ethylene-compounds to resolve themselves, in presence of alkalies, into vinyl-compounds, it appeared not improbable that a fourth series of bodies would likewise be formed, viz.—

$$[(C_2H_3)\ H_3N]Br,$$
$$[(C_2H_3)_2H_2N]Br,$$
$$[(C_2H_3)_3H\ N]Br,$$
$$\text{and } [(C_2H_3)_4\quad N]Br;$$

and thus was presented the not very inviting problem of separating from a great mass of bromide of ammonium, no fewer than sixteen different bases.

In the experiments on the action of dibromide of ethylene on ammonia and its homologues, which I hope to lay before the Royal Society in a special paper, I have indeed by no means met with the whole of these compounds; but in place of the deficient members of the groups, new products have made their appearance, whose formation in the present state of our knowledge could scarcely have been predicted. Without entering into details respecting these products, I will merely observe that I was induced, by the complication of this reaction, to subject dibromide of ethylene to the action of ethylamine, diethylamine, and finally of triethylamine instead of ammonia; for it could not be doubted that with the progressive substitution of ethyl for the hydrogen in ammonia, the process would be simplified, the number of possible products of reaction being considerably diminished. Ammonia indeed—omitting secondary products—is capable of producing not less than *sixteen* compounds, whereas ethylamine cannot yield

more than *twelve*, diethylamine not more than *eight*, and, lastly, in the reaction between triethylamine and dibromide of ethylene the number of compounds possible under the most favourable circumstances is limited to *four*. Experiment has verified this anticipation; in the same proportion as the substitution advances in the ammonia submitted to the action, the number of products generated diminishes; nevertheless, the experiment with triethylamine, from which I had expected the simplest and clearest solution of my problem, did not entirely satisfy me, inasmuch as I did not succeed in obtaining more than *three* of the compounds out of the *four* which are indicated by theory. It was not indeed till I repeated the experiment in the phosphorus-series, using, instead of triethylamine, the corresponding phosphorus-base, that I succeeded in obtaining *all* the compounds, and that the results appeared as the pure expression of theory, undisturbed by accidental products. In its reaction with dibromide of ethylene, the sharply defined characters of triethylphosphine exhibit themselves with welcome distinctness; and in the products resulting from the action, the peculiar relations between monatomic and diatomic bases become perceptible with a degree of clearness and generality such as I have never observed in any similar reaction among bodies of the nitrogen-series. It is the smoothness of these reactions which renders it desirable to commence an account of a more general investigation of the diatomic bases with a description of the bodies belonging to the phosphorus-series.

ETHYLENE-GROUP.

Action of Dibromide of Ethylene on Triethylphosphine.

When these two bodies are brought together in quantities not too large, the liquid becomes turbid, but no rise of temperature takes place to indicate the occurrence of chemical action. The mixture, after being left to itself for a few hours, deposits white crystals, the formation of which continues till the entire liquid is converted into a white saline mass. If the mixture be even gently heated, the crystallization takes place instantaneously, and a violent reaction sets in, which is very apt to project a portion of the resulting salt from the vessel. In operating on rather a large scale in vessels filled with air, the heat evolved on agitation, in consequence of the oxidation of the phosphorus-base, is often sufficient to start the reaction.

In preparing considerable quantities of the white crystals, I have therefore found it convenient to add to the triethylphosphine twice its volume of ether, to mix the ethereal solution with the dibromide of ethylene in a flask filled with carbonic acid gas, and to heat the mixture in a water-bath, the flask being provided with an inverted cooling apparatus, so that the vapours which escape may be condensed and returned. Or, the mixture of triethylphosphine, dibromide of ethylene and ether may be introduced into long tubes previously drawn out, and the tubes, after sealing, be immersed for some hours in boiling water. As the value of dibromide of ethylene is trifling in comparison with

that of triethylphosphine, I always used, in commencing the study of this reaction, the former substance in excess. The triethylphosphine is quickly fixed by the dibromide of ethylene, and the action may be considered as terminated when the presence of the free phosphorus-base in the mixture is no longer indicated by disulphide of carbon. As soon as this point is attained, the crystalline bromides may be thrown on a filter, the ether allowed to run off, and the crystals freed from excess of bromide of ethylene by washing them for a while with anhydrous ether, in which they are quite insoluble.

The crystals thus obtained dissolve with great facility in water and in ordinary alcohol, somewhat less readily in boiling absolute alcohol. This solution on cooling deposits well-developed crystals, which sustain a heat of 100° without decomposition, but show a slight tendency to deliquesce in the air. The analysis of these crystals, and their behaviour with reagents, showed unmistakeably that, in the action of dibromide of ethylene on triethylphosphine, two bromides at least are formed. The determination of the bromine by means of nitrate of silver in the products of different preparations, purified by successive crystallizations from alcohol, gave the following percentages of bromine:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Bromine . .	32·10	29·58	28·30	28·05	27·46	27·30	27·15	26·85	25·94.

On again repeating the crystallization, the amount of bromine precipitated by nitrate of silver did not exhibit any further diminution.

The complete analysis of the crystals, purified by a great number of crystallizations from alcohol, which will be given in a subsequent paragraph of the paper, has led me to the simple expression

$$C_8 H_{19} P Br_2 = C_6 H_{15} P + C_2 H_4 Br_2,$$

whence it appears that the body is produced by the combination of one molecule of triethylphosphine with one molecule of the bromine-compound.

The purification of the second substance, yielding with nitrate of silver a larger proportion of bromine, which remains in the mother-liquor of the compound just described, is somewhat complicated. As I shall have to return to this body in the description of the individual compounds, I content myself in this place with just setting forth the general character of the reaction by quoting the formula deduced from its examination. The analysis of this bromine-compound, together with those of a whole series of bodies derived from it, has led to the formula

$$C_{14} H_{34} P_2 Br_2 = 2 C_6 H_{15} P + C_2 H_4 Br_2,$$

showing that the body is a compound of two molecules of triethylphosphine and one molecule of dibromide of ethylene.

These observations are sufficient to establish the peculiar nature of the reaction in question. There are clearly two successive phases to be distinguished, according as the bromide of ethylene lays hold of one or two molecules of triethylphosphine; secondary products may likewise be formed, which for the present may be left out of consideration,

as I shall have to allude to them in the course of the memoir. It is, however, worth while to mention in this place that, when the experiment is made with pure substances, and under the conditions above mentioned, the two bromides described are almost the only products of the reaction.

These two bodies have become the starting-points of two extensive groups of compounds, which may even now be distinguished as the *series of monatomic compounds*, and the *series of diatomic compounds*.

I now proceed to the detailed description of the individual members of these series.

SERIES OF MONATOMIC COMPOUNDS. MONOPHOSPHONIUM COMPOUNDS.

Salts of Bromethyl-triethylphosphonium.

Bromide of Bromethyl-triethylphosphonium.—By this long name I designate the crystalline substance which is produced by the union of one molecule of dibromide of ethylene and one molecule of triethylphosphine. The preparation of this compound has already been given in the preceding paragraph. It is the chief product of the reaction when the dibromide of ethylene is in excess.

The equation

$$C_2H_4Br_2 + C_6H_{15}P = C_8H_{19}PBr_2$$

requires about 1 vol. of dibromide of ethylene to 1·5 vol. of triethylphosphine; but even when a larger quantity of the bromine-compound is *heated* with the phosphorus-base, both in presence or absence of ether or alcohol, we always obtain an appreciable quantity of the second bromide. It is only by allowing an *immense* excess of dibromide to act at the *common temperature* upon triethylphosphine, either in presence or absence of ether, that the formation of the second bromide is altogether avoided. In this reaction, which is not complete in less than twenty-four hours, a considerable quantity of gas is evolved, which does *not* appear when the substances are heated together.

To purify a product, which contains appreciable quantities of the second bromide, it is necessary to crystallize it at least three or four times from absolute alcohol; in the last crystallization it is desirable to mix the alcoholic solution with a moderate quantity of ether. The solution, if left to itself, frequently deposits separate well-defined crystals, which may be dried without decomposition at 100°, and which melt at about 235° with partial decomposition, hydrobromic acid being abundantly evolved. The bromide, purified in the manner just described, gave on analysis the following numbers:—

I. 0·5630 grm. of bromide gave 0·6521 grm. of carbonic acid and 0·3173 grm. of water.

II. 0·4926 grm. of bromide, precipitated by nitrate of silver, gave 0·3004 grm. of bromide of silver.

A simple experiment showed that nitrate of silver precipitates from this compound

only part of the bromine. When the liquid filtered from the precipitated bromide of silver was mixed with carbonate of sodium, to remove the excess of silver, and evaporated, the residue, when ignited with lime and dissolved in nitric acid, gave, on addition of nitrate of silver, a fresh quantity of bromide of silver. I therefore endeavoured to obtain the entire quantity of bromine by means of recently precipitated oxide of silver, a process which I had previously found serviceable in similar cases. The result confirmed my anticipation. Digestion with oxide of silver removes the whole of the bromine, and shows that the quantity precipitated by nitrate of silver is only half the total amount.

III. 1·8445 grm. of bromide digested with oxide of silver, gave, after the removal of the excess of oxide of silver by nitric acid, 2·2635 grm. of bromide of silver.

These numbers lead to the formula

$$C_8 H_{19} P Br_2,$$

as seen from the following comparison:—

	Theory.			Experiment.		
				I.	II.	III.
C_8	96	31·37		31·59	——	——
H_{19}	19	6·21		6·26	——	——
P	31	10·14		——	——	——
Br	80	26·14	52·28	——	25·94	52·22
Br	80	26·14		——	——	
	306	100·00				

The interpretation of these results presents no difficulty. The crystals are evidently the bromide of a monophosphonium in which 3 equivs. of ethyl are substituted for 3 equivs. of hydrogen, the last equivalent of hydrogen being replaced by a secondary radical, $C_2 H_4 Br$, which for the present I will call monobrominated ethyl or bromethyl.

The molecular formula

$$[(C_2 H_4 Br)(C_2 H_5)_3 P] Br$$

represents the constitution of this salt.

I have already observed that this bromide is occasionally obtained in well-defined crystals. They were examined by Quintino Sella, who has sent me the following description:—

"System monometric (regular).

The crystals exhibit the form of the rhombic dodecahedron 1 1 0 (Fig. 28). They are sometimes elongated so as to present the aspect of dimetric crystals, as in Fig. 29. Sometimes it even happens that one of the faces $\bar{1}$ 1 0 is much more developed than the parallel face 1 $\bar{1}$ 0 (Fig. 30), so that scarcely more than half the crystal (Fig. 29) appears to exist. Sometimes the faces exhibit striæ parallel to the adjacent edges of the rhombic dodecahedron.

Fig. 28.

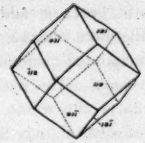


Fig. 29.

Fig. 30.

Lustre fatty.

Hardness inferior to that of gypsum.

The crystals have no action on polarized light."

By treating the bromide with silver-salts *in the cold*, the bromine external to the phosphonium-metal is replaced by the acid-radical united with the silver, while the bromine belonging to the phosphonium remains untouched. In this manner we obtain the salts of the new metal, which exhibit an inclination to unite with excess of the silver-salt, in the form of double compounds. The *chloride* and the *nitrate* prepared from the bromide by the action of chloride and nitrate of silver are extremely soluble in water and alcohol, and crystallize indistinctly. The *sulphate* forms long white crystalline needles, likewise very soluble in water and alcohol. It is very easily obtained by the action of sulphuretted hydrogen on the double salt which is formed by treating the bromide with sulphate of silver; on adding alcohol and ether to the concentrated liquid containing free sulphuric acid, it is precipitated in crystals. The sulphate, treated with iodide of barium, yields the *iodide*, a salt which dissolves sparingly in water, and crystallizes in scales of a pearly lustre.

I have not examined these salts more particularly, as they scarcely present any theoretical interest, and as the composition of the bromide, which forms the starting-point of the series, is sufficiently corroborated by the analysis of the platinum- and gold-salts.

Platinum-salt.—The chloride obtained by digesting the bromide with excess of chloride of silver is mixed with dichloride of platinum, when the platinum-salt is deposited on cooling in light orange-yellow prisms, frequently an inch in length. This salt is somewhat sparingly soluble in cold, more readily in boiling water, and may be crystallized without decomposition. During the recrystallizations, this salt, under circumstances not yet clearly made out, is occasionally obtained in crystals of an octohedral habitus.

This platinum-salt, though somewhat sparingly soluble, is nevertheless essentially different from the platinum-salt of the diphosphonium to be described hereafter, which accompanies the bromethyl-triethylphosphonium. The latter is nearly insoluble in water, and is precipitated from the most dilute solutions. This character forms a means of testing the purity of the monophosphonium-bromide in the succession of crystallizations to which it has to be submitted for the sake of purification. The salt is pure when the dilute solution, after being treated with chloride of silver, no longer gives a precipitate with dichloride of platinum.

I. 0·4593 grm. of platinum-salt gave 0·3854 grm. of carbonic acid and 0·1880 grm. of water.

II. 0·5397 grm. of platinum-salt gave 0·4515 grm. of carbonic acid and 0·2157 grm. of water.

III. 0·549 grm. of platinum-salt, fused with carbonate of sodium, gave 0·785 grm. of a mixture of bromide and chloride of silver and 0·1253 grm. of platinum.

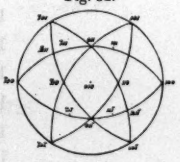
These numbers fix the formula

$$C_8 H_{19} Br P Pt Cl_3 = [(C_2 H_4 Br)(C_2 H_5)_3 P] Cl, Pt Cl_2.$$

	Theory.			Experiment.		
				I.	II.	III.
C_8	96	22·26		22·88	22·81	——
H_{19}	19	4·41		4·55	4·44	——
P	31	7·19		——	——	——
Br	80	18·55	43·25	——	——	43·11*
Cl_3	106·5	24·70		——	——	
Pt	98·7	22·89		——	——	22·82
	431·2	100·00				

As I have already mentioned, this platinum-salt can easily be obtained in fine long needles; they exhibit, however, but rarely well-formed terminal faces. Only once I succeeded in getting them somewhat better developed. These crystals were examined by Quintino Sella with the following results:—

Fig. 31.



"System monoclinic:—

100, 101=55° 59′; 001, 101=33° 3′; 010, 111=60° 37′.

Forms observed:—

100, 010, 110, 101, $\bar{1}01$, 011, 111, $\bar{1}11$, $\bar{2}11$ (Fig. 31).

Angles.		Calculated.	Observed.
		° ′	° ′
100, 010	=	90 0	——
100, 110	=	45 55	45 57
100, 101	=	55 59	55 51
100, $\bar{1}01$	=	122 40	122 40
100, 011	=	89 12	89 12
100, 111	=	60 50	61 1
100, $\bar{1}11$	=	117 56	117 50
100, $\bar{2}11$	=	137 4	136 54

* With the admissible assumption that the compound contains 3 equivs. of chlorine for 1 equiv. of bromine.

Angles.		Calculated.	Observed.
		° ′	° ′
010, 110	=	44 5	——
010, 101	=	90 0	——
010, $\bar{1}$01	=	90 0	——
010, 011	=	55 49	55 49
010, 111	=	60 37	——
010, $\bar{1}$11	=	60 14	——
010, $\bar{2}$11	=	67 30	——
110, $\bar{1}$10	=	88 11	88 7
110, 101	=	67 6	67 8
110, $\bar{1}$01	=	112 3	111 53
110, 011	=	65 35	65 29
110, 01$\bar{1}$	=	66 48	66 50
110, 111	=	46 15	46 6
110, $\bar{1}$1$\bar{1}$	=	89 14	——
110, $\bar{1}$11	=	88 15	——
110, 11$\bar{1}$	=	46 57	——
110, $\bar{2}$11	=	103 33	——
110, 21$\bar{1}$	=	38 21	——
101, $\bar{1}$01	=	66 41	66 49
101, 011	=	46 6	46 2
101, 111	=	29 23	29 18
101, $\bar{1}$11	=	69 54	——
101, $\bar{2}$11	=	86 42	——
$\bar{1}$01, 011	=	46 28	46 24
$\bar{1}$01, 111	=	69 49	——
$\bar{1}$01, $\bar{1}$11	=	29 46	——
$\bar{1}$01, $\bar{2}$11	=	29 36	——
011, 01$\bar{1}$	=	111 38	111 37
011, 111	=	28 22	28 11
011, $\bar{1}$1$\bar{1}$	=	109 11	——
011, $\bar{1}$11	=	28 44	28 36
011, 11$\bar{1}$	=	108 36	——
011, $\bar{2}$11	=	47 52	47 42

Angles.		Calculated.	Observed.
		° ′	° ′
$011, 21\bar{1}$	=	103 56	——
$111, \bar{1}1\bar{1}$	=	121 14	121 23
$111, \bar{1}11$	=	57 7	56 49
$111, 11\bar{1}$	=	93 12	——
$111, \bar{2}11$	=	76 14	75 53
$111, 21\bar{1}$	=	82 5	——
$\bar{1}11, 11\bar{1}$	=	120 28	——
$\bar{1}11, \bar{2}11$	=	19 7	19 4
$\bar{1}11, 21\bar{1}$	=	124 23	——
$\bar{2}11, 21\bar{1}$	=	134 59	——

According to NAUMANN:—

$$a:b:c=0{\cdot}6580:1:0{\cdot}9685;\quad \gamma=89°\,2'.$$

Forms observed:—

$$\infty P\,\infty,\ \infty P\infty,\ \infty P,\ P\infty,\ -P\infty,\ P\infty,\ P,\ -P,\ 2P2.$$

According to WEISS:—

$$a:b:c=1:0{\cdot}9685:0{\cdot}6580;\quad a\,o\,c=90°\,58'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:b:\infty c;\quad a:b:\infty c;\quad a:\infty b:c;\quad -a:\infty b:c;$$
$$\infty a:b:c;\quad a:b:c;\quad -a:b:c;\quad -\tfrac{1}{2}a:b:c.$$

According to LEVY:—

$$M\,M=88°\,11';\quad M\,P=90°\,40;\quad b:h=1:0{\cdot}4726.$$

Forms observed:—

$$h',\ g',\ M,\ o',\ a',\ e',\ d^{\frac{1}{2}},\ b^{\frac{1}{2}},\ a_3.$$

Fig. 32.

Fig. 33.

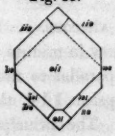
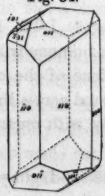


Fig. 34.



Combinations observed:—

110, 011, 100; 101, $\bar{1}01$ (Figs. 32, 33).
110, 011; 100, $\bar{1}11$, $\bar{1}01$ (Fig. 34).
110, 011; 100, $\bar{1}11$, $\bar{1}01$, $\bar{2}11$ (Fig. 35).
110, $\bar{1}11$; 100, $\bar{1}01$, 011, 111 (Fig. 36).
110, 011; 100, 111; 101, $\bar{1}11$, $\bar{2}11$ (Fig. 37).
110, 011, 100; 010, 011, $\bar{1}01$, $\bar{2}11$ (Figs. 38, 39).

Fig. 35.

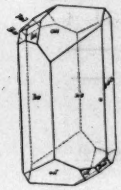
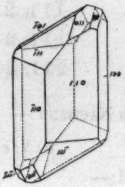


Fig. 36.



The faces 011 are often very unequally developed, as seen in Figs. 32 and 33, and in Figs. 38 and 39; under these circumstances some of the faces of the forms 111, $\bar{1}11$, $\bar{2}11$ are apt to disappear, as may be seen in Figs. 38 and 39.

Fig. 37.

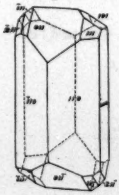
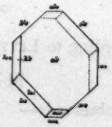


Fig. 38.

Fig. 39.



Cleavages: 100, 110. Lustre: vitreous.

Colour: orange with a tint of yellow in minute, and of red in larger, crystals.

The plane of the optical axes is parallel to the axis of symmetry [010], for rings are observed across the faces of the prism 110, the centres of which are disposed symmetrically with regard to [010]. The principal medium-line is perpendicular to [010]."

Gold-salt.—Light yellow needles, difficultly soluble in cold water, recrystallizable from boiling water.

0·2394 grm. of gold-salt left on ignition 0·0841 grm. of gold.

The formula

$$C_8H_{19}BrPAuCl_4 = [(C_2H_4Br)(C_2H_5)_3P]Cl,\ AuCl_3$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium . . .	226	40·00	——
4 equivs. of Chlorine	142	25·13	——
1 equiv. of Gold	197	34·87	35·12
1 equiv. of Gold-salt	565	100·00	

I have in vain endeavoured to prepare the hydrate

$$C_8H_{20}BrPO = \left.\begin{matrix}[(C_2H_4Br)(C_2H_5)_3P] \\ H\end{matrix}\right\}O$$

belonging to these salts.

In quoting the analysis of the bromide, I have already mentioned that this salt, when treated with oxide of silver, gives up the whole of its bromine. On mixing the caustic liquid filtered from the silver-salt with hydrochloric acid and dichloride of platinum, we no longer obtain the sparingly soluble platinum-salt crystallizing in the characteristic needles; but the liquid, after being considerably concentrated by evaporation, yields well-defined, reddish-yellow octohedra belonging to another base. An exactly similar result is obtained on attempting to separate the base from the sulphate by means of baryta. After filtering off the sulphate of barium, there remains a strongly alkaline liquid, which likewise yields only the octohedral platinum-salt, while the presence of bromide of barium in the solution indicates the transformation of the original molecular system. The elimination of the second equivalent of bromine by silver-salts, which takes place instantly and completely in alkaline liquids, may likewise be effected by continual ebullition in neutral and even in acid solutions, though always slowly and incompletely. If the bromide be precipitated by excess of nitrate of silver, the filtered liquid, on being boiled and evaporated, deposits a fresh quantity of bromide of silver; but in most cases, even after long-continued boiling, a considerable quantity of bromine remains latent, and may be immediately recognized by again filtering the liquid and slightly supersaturating it with ammonia, the whole of the remaining bromine being then precipitated as bromide of silver. This deportment furnishes in fact a characteristic distinction of the bromethylated bromide, by which this substance may often be conveniently recognized. It deserves to be remarked that the fixed caustic alkalies exert but a slight action on the bromethylated bromide; the compound is precipitated by the alkalies from its cold aqueous solution in the crystalline state and without decomposition, and it is only after some time that alterations take place, probably affecting its intimate constitution. The nature of these alterations has not yet been made out. The crystals may be boiled for some time with alcoholic solution of potassa without decomposition. The bromide likewise suffers no alteration by continued digestion with water or alcohol at 100°.

Salts of Oxethyl-triethylphosphonium.

Iodide.—When the caustic liquid produced by treating the bromide of bromethyl-triethylphosphonium with oxide of silver is neutralized with hydriodic acid and the solution evaporated, an iodide is obtained which crystallizes in needles, and dissolves very readily in water and alcohol. The finest crystals are obtained by mixing the alcoholic solution with ether till it becomes opalescent, and then allowing it to crystallize. If too much ether has been added, the new iodide is precipitated as an oil, which solidifies but slowly to a crystalline mass. The salt becomes coloured at 100°, and must therefore be dried *in vacuo*.

I. 0·3003 grm. of iodide gave 0·3615 grm. of carbonic acid and 0·1890 grm. of water.
II. 0·4665 grm. of iodide gave 0·5760 grm. of carbonic acid and 0·2832 grm. of water.
III. 0·3705 grm. of iodide gave 0·2990 grm. of iodide of silver.
IV. 0·2970 grm. of iodide gave 0·2427 grm. of iodide of silver.
V. 0·4080 grm. of iodide gave 0·3344 grm. of iodide of silver.

These numbers lead to the formula

$$C_8H_{20}OPI = [(C_2H_5O)(C_2H_5)_3P]I,$$

which requires the following values:—

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
C_8	96	33·10	32·84	33·67	——	——	——
H_{20}	20	6·90	6·99	6·74	——	——	——
O	16	5·51	——	——	——	——	——
P	31	10·69	——	——	——	——	——
I	127	43·80	——	——	43·62	44·16	44·28
	290	100·00					

The transformation of the bromethylated phosphonium takes place, therefore, exactly as might be expected from analogy, the bromine being eliminated as bromide of silver, and its place being taken by the molecular residue of the water:—

$$[(C_2H_4Br)(C_2H_5)_3P]Br + Ag_2O + H_2O = 2AgBr + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\ H\end{matrix}\right\}O.$$

Hydrate.—The caustic solution of the oxide exhibits the usual characteristic properties of this class of bodies. Over sulphuric acid, the solution thickens to a syrupy, extremely deliquescent mass, from which the base separates in oily drops on addition of potassa. Its decomposition by heat is characteristic; at a rather high temperature, it is resolved into oxide of triethylphosphine, ethylene, and water:—

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\ H\end{matrix}\right\}O = (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The oxide of triethylphosphine was identified by the preparation of its platinum-salt; the ethylene, by converting it into the bromide.

The above equation represents the final result of the action of heat; this final result, however, is preceded by several intermediate changes, to which I shall return in a subsequent chapter of this paper.

Bromide.—Extremely soluble. Dries up over sulphuric acid to an indistinct crystalline mass.

Chloride.—This compound resembles the bromide in every respect. Both these salts readily form double compounds with iodide and bromide of zinc. The chloride, under the influence of pentabromide and pentachloride of phosphorus, undergoes remarkable transformations, to which I shall presently recur.

Perchlorate.—Laminæ somewhat sparingly soluble in cold water.

I have not analysed any of these salts, inasmuch as the composition of this series of compounds is sufficiently established by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—The alkaline solution, from which the iodide was obtained, yields, when saturated with hydrochloric acid, mixed with dichloride of platinum, and evaporated, the above-mentioned platinum-salt, crystallizing in well-developed octohedra, the measurements of which I subjoin. It is easily soluble in hot water, and may be recrystallized without decomposition.

Its composition is

$$C_8 H_{20} O P Pt Cl_3 = [(C_2 H_5 O)(C_2 H_5)_3 P] Cl, Pt Cl_2,$$

as appears from the following analysis:—

I. 0·4626 grm. of platinum-salt gave 0·4510 grm. of carbonic acid and 0·2217 grm. of water.

II. 0·5278 grm. of platinum-salt, when fused with carbonate of sodium, gave 0·1408 grm. of platinum and 0·6175 grm. of chloride of silver.

III. 0·5195 grm. of platinum-salt gave 0·1405 grm. of platinum and 0·6110 grm. of chloride of silver.

IV. 1·3105 grm. of platinum-salt, precipitated with hydrosulphuric acid, gave 0·3522 grm. of platinum.

The several salts analysed were of different preparations. The specimen submitted to analysis IV. was obtained under particular conditions, to which I shall return hereafter.

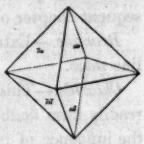
	Theory.		Experiment.			
			I.	II.	III.	IV.
C_8	96	26·07	26·58	——	——	——
H_{20}	20	5·43	5·32	——	——	——
O	16	4·35	——	——	——	——
P	31	8·42	——	——	——	——
Pt	98·7	26·81	——	26·68	27·04	26·87
Cl_3	106·5	28·92	——	28·94	29·08	——
	368·2	100·00				

The following are the details of QUINTINO SELLA's measurements:—

"System monometric:—

Forms observed:—

Fig. 40.



111 (Fig. 40).

Angles.	Calculated.	Observed.
$111, 11\bar{1}$	= 70° 32′	70° 7′
$11\bar{1}, \bar{1}1\bar{1}$	= 70 32	70 33
$\bar{1}1\bar{1}, \bar{1}11$	= 70 32	70 16
$\bar{1}11, 111$	= 70 32	71 4
$111, \bar{1}1\bar{1}$	= 109 28	109 32
$\bar{1}11, 11\bar{1}$	= 109 28	109 44

The octohedra are generally very minute. The crystals have no sensible influence on polarized light. Colour orange."

Gold-salt.—Golden-yellow needles, sparingly soluble in cold, readily in boiling water; in a quantity of boiling water not sufficient to dissolve them, they fuse to a transparent yellow oil. Not decomposed by recrystallization. Precipitated by trichloride of gold from a moderately concentrated solution of the chloride.

0·630 grm. of gold-salt, precipitated with hydrosulphuric acid, &c., gave 0·2475 grm. of gold.

The formula

$$C_8H_{20}OPAuCl_4 = [(C_2H_5O)(C_2H_5)_3P]Cl, AuCl_3$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium .	163	32·48	——
4 equivs. of Chlorine . . .	142	28·28	——
1 equiv. of Gold	197	39·24	39·28
1 equiv. of Gold-salt . . .	502	100·00	

I have already alluded to the decomposition which the chloride of the oxethylated phosphonium undergoes under the influence of pentabromide of phosphorus. The two bodies act upon one another with great violence; oxybromide of phosphorus and hydrobromic acid are evolved, and the residue is found to contain the chloride of the bromethylated phosphonium from which the oxethylated compound was originally produced.

$$[(C_2H_5O)(C_2H_5)_3P]Cl + PBr_5 = POBr_3 + HBr + [(C_2H_4Br)(C_2H_5)_3P]Cl.$$

Nothing is easier than to obtain experimental proof of this transformation, which is of considerable theoretical interest. After the oxybromide and the excess of pentabromide have been removed as completely as possible by evaporation, the remaining liquid yields, on addition of dichloride of platinum, a sparingly soluble, still impure platinum-salt, which, after washing, may be decomposed by sulphuretted hydrogen and thereby

purified. If the chloride thus formed be precipitated with excess of nitrate of silver, and the nitrate of the base, filtered from the chloride of silver, be mixed with ammonia and gently heated, a copious precipitate is immediately formed, consisting of bromide of silver. This reaction is characteristic of the bromethylated body. Moreover, on mixing the solution of the nitrate freed from silver with dichloride of platinum, and recrystallizing the platinum-precipitate from boiling water, the liquid yields on cooling the splendid needles of the platinum-salt of the bromethylated triethylphosphonium. The analysis of this salt was omitted, partly because no doubt could be entertained respecting its nature, and partly because I had occasion to establish by a number—as will be noticed hereafter—the nature of the precisely similar reaction between chloride of oxethyl-triethylphosphonium and pentachloride of phosphorus.

Thus it is seen that the molecular group C_2H_5O, which is supposed to replace the hydrogen in the salt, suffers, under the influence of pentabromide of phosphorus, alterations exactly similar to those which it would have undergone under similar circumstances when conceived as a constituent of alcohol.

If we consider the facility with which the bromethylated phosphonium is converted into the oxethylated compound by the action of oxide of silver, and the simple re-formation of the first-mentioned body by means of pentabromide of phosphorus, a great variety of new experiments suggest themselves. In reviewing the relations which obtain between the bromethylated and oxethylated phosphoniums, who could fail to perceive that the two hydrogen-replacing radicals, which constitute the difference between these two organic metals, stand to one another in the same relation as bromide of ethyl and alcohol, or bromide of acetyl and acetic acid? But if this be so, what a number of new bodies does this consideration bring into view, even if we limit our calculation to the transformations of which the molecular group C_2H_5O in alcohol is susceptible! As yet I have scarcely penetrated into this new field of inquiry, and I must be satisfied to quote a single experiment, which exhibits the above-mentioned bodies in a new light. The salts of bromethylated and oxethylated triethylphosphonium may be regarded as tetrethylphosphonium salts, in which an atom of hydrogen is replaced by bromine and the radical HO respectively:

Bromide of tetrethylphosphonium	$[(C_2H_4H)(C_2H_5)_3P]Br$,
Bromide of bromethylated triethylphosphonium .	$[(C_2H_4Br)(C_2H_5)_3P]Br$,
Bromide of oxethylated triethylphosphonium . .	$[(C_2H_4HO)(C_2H_5)_3P]Br$;

and the question arose whether the bromethylated salt might not be converted by a simple process into the tetrethylphosphonium-compound. This transformation may indeed be effected without the slightest difficulty. On acidulating the solution of the bromethylated bromide with sulphuric acid, and digesting it with granulated zinc, the bromine is eliminated in the form of hydrobromic acid, its place being filled up by one equivalent of hydrogen:

$$|(C_2H_4Br)(C_2H_5)_3P]Br + H_2 = HBr + [(C_2H_5)_4P]Br.$$

By decanting the liquid from the excess of zinc and treating it with oxide of silver, oxide of zinc, bromine and sulphuric acid are removed, and a solution of oxide of tetrethylphosphonium is obtained, which, when mixed with hydrochloric acid and dichloride of platinum, yields well-developed octohedra of the platinum-salt of tetrethylphosphonium.

0·444 grm. of this salt, decomposed by hydrosulphuric acid, yielded &c., 0·1240 grm. of platinum.

The formula

$$C_8 H_{20} P Pt Cl_3 = [(C_2 H_5)_4 P] Cl, Pt Cl_2$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Tetrethylphosphonium .	147·0	41·75	——
1 equiv. of Platinum	98·7	28·02	27·93
3 equivs. of Chlorine	106·5	30·23	——
1 equiv. of Platinum-salt	352·2	100·00	

The chloride obtained in the analysis was converted, by successive treatment with oxide of silver and hydriodic acid, into the corresponding iodide. This characteristic salt appeared on careful comparison exactly similar to the iodide of tetrethylphosphonium prepared in the ordinary way.

Here, then, we have an instance of the direct reproduction of an ethyl-compound from a body of the ethylene-group by a simple process of reduction. Similar transformations would doubtless succeed in many other cases, and this is perhaps a fitting opportunity of directing attention to the interest which the employment of this reaction would have in connexion with the intermediate hydrochloric glycol-ether discovered by Wurtz. Probably this compound, when subjected to the action of nascent hydrogen, would be directly converted into alcohol:

$$(C_2 H_4)'' \left\{ \begin{matrix} H \\ Cl \end{matrix} \right. O = C_2 H_5 Cl O,$$

$$(C_2 H_4)'' \left\{ \begin{matrix} H \\ H \end{matrix} \right. O = C_2 H_6 O;$$

and when considered with reference to this decomposition, would appear as monochlorinated alcohol.

It was chiefly the facility with which a tetrethylphosphonium-compound may be obtained from the bromethylated bromide that induced me to designate the hydrogen-replacing molecules $C_2 H_4 Br$ and $C_2 H_5 O$, which we meet in the compounds above described, as *bromethyl* and *oxethyl*. I was anxious to submit the ideas which guided me in the selection of these terms to the test of experiment. We know from the experiments of Regnault, that dichloride of ethylene and monochlorinated chloride of ethyl are essentially different bodies; and not less distinct are dibromide of ethylene and monobrominated bromide of ethyl, which I have obtained in the course of these experi-

ments by the action of bromine on bromide of ethyl. But, on the other hand, the allied members of these two pairs of bodies are so closely related to each other, that, under the influence of powerful reagents, they not unfrequently yield exactly the same products of transformation. I may here refer especially to an interesting experiment of BEILSTEIN, who has shown that dichloride of ethylene and monochlorinated chloride of ethyl, when treated with alcoholic potassa, undergo the same decomposition: both these compounds give up hydrochloric acid, being converted into chloride of vinyl.

The denomination, *bromethyl-triethylphosphonium*, which I have adopted for the metal produced by the action of dibromide of ethylene on triethylphosphine, involves to a certain extent the assumption that this body might also, under favourable circumstances, be produced by the mutual action of triethylphosphine and monobrominated bromide of ethyl. In a subsequent chapter of this inquiry I shall have an opportunity of showing how far this assumption is established by experiment.

SALTS OF VINYL-TRIETHYLPHOSPHONIUM.

In tracing the history of the salts of bromethyl-triethylphosphonium, I have mentioned that these substances lose their latent bromine, though slowly, when boiled with silver-salts. I was curious to ascertain whether this reaction involves the same metamorphosis which the bromethylated body undergoes under the influence of oxide of silver.

In the anhydrous condition, the bromethylated bromide acts but slowly on acetate of silver. In the presence of alcohol or water, the reaction is soon accomplished at 100° C. The liquid filtered from the bromide of silver yields no further precipitate on addition of ammonia, showing that the whole of the bromine is eliminated. When evaporated with hydrochloric acid, the liquid abundantly evolves acetic acid. After sufficient concentration, it yields with dichloride of platinum a fine octohedral salt, which may be purified by crystallization.

I. 0·4222 grm. of platinum-salt gave 0·4203 grm. of carbonic acid and 0·2017 grm. of water.

II. 0·4215 grm. of platinum-salt of a new preparation gave 0·4267 grm. of carbonic acid and 0·1990 grm. of water.

III. 0·9430 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·2660 grm. of platinum.

IV. 0·7115 grm. of platinum-salt gave 0·2015 grm. of platinum.

V. 0·3625 grm. of platinum-salt gave 0·1020 grm. of platinum.

VI. 0·6354 grm. of platinum-salt gave 0·1785 grm. of platinum.

VII. 0·5585 grm. of platinum-salt gave 0·1590 grm. of platinum.

VIII. 0·3675 grm. of platinum-salt gave 0·1025 grm. of platinum and 0·451 grm. of chloride of silver.

The percentages derived from these experiments characterize the compound

$$C_8 H_{18} P Pt Cl_3 = [(C_2 H_3)(C_2 H_5)_3 P] Cl, Pt Cl_2,$$

which requires the following values:—

	Theory.		Experiment.							
			I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C_8	96	27·41	27·15	27·61	——	——	——	——	——	——
H_{18}	18	5·14	5·30	5·24	——	——	——	——	——	——
P	31	8·85	——	——	——	——	——	——	——	——
Pt	98·7	28·19	——	——	28·20	28·33	28·13	28·09	28·47	27·89
Cl_3	106·5	30·41	——	——	——	——	——	——	——	30·39
	350·2	100·00								

It is thus seen that the action of silver-salts—at all events of acetate of silver—upon the bromethylated bromide differs from that of oxide of silver. While the latter gives rise to the formation of an oxethylated phosphonium, the former produces a phosphoretted metal in which three atoms of ethyl are associated with one atom of the radical C_2H_3, which may be termed vinyl. The product, then, which is formed by the action of acetate of silver upon the bromethylated bromide is the acetate of vinyl-triethylphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + 2\left(\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O\Big) = 2\,AgBr + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\[(C_2H_3)(C_2H_5)_3P]\end{matrix}\right\}O.$$

I have been satisfied to establish the formation and composition of the vinyl-compound by a careful and frequently repeated analysis of the platinum-salt, which had been obtained from the products of four different operations. The salts of vinyl-triethylphosphonium resemble the oxethylated compounds. I have prepared the iodide, which crystallizes, but is extremely soluble even in absolute alcohol.

I have observed the formation of vinyl-compounds in several other processes, which may here be briefly mentioned, although I must state at once that the experimental evidence on which these observations are based is less conclusive.

The oxethylated compound differing from the vinyl-triethylphosphonium-salt simply by the elements of one molecule of water, which the latter contains less, the question naturally suggested itself whether, under the influence of heat, the oxethylated compound might not be converted into the vinyl-body. The results of two experiments appear to answer this question in the affirmative. In one case the bromide of bromethyl-triethylphosphonium had been boiled for a considerable time with oxide of silver. The product of the reaction, converted into a platinum-salt, gave the following numbers:—

I. 0·6956 grm. of platinum-salt, ignited with carbonate of sodium, gave 0·1985 grm. of platinum and 0·8528 grm. of chloride of silver.

In another experiment, performed chiefly with the view of studying the action of heat upon the oxethylated base, a concentrated solution of the latter was evaporated in a capsule over an open flame until a very appreciable quantity was entirely decomposed. The residue was saturated with hydrochloric acid and precipitated with dichloride of platinum. A difficultly soluble amorphous platinum-salt was thrown down, at which I

shall glance again in a subsequent chapter of this paper, and the mother-liquor furnished an octohedral platinum-salt, which was crystallized from boiling water and submitted to analysis.

II. 0·4180 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1180 grm. of platinum.

These numbers characterize the vinyl-compound.

	Vinyl-compound.	Oxethyl-compound.	Experiment. I.	Experiment. II.
Platinum	28·19	26·81	28·53	28·23
Chlorine	30·41	28·92	30·33	——

I must, however, add at once, that I failed to reproduce this result in repeating the experiment in a somewhat different manner. Oxide of oxethyl-triethylphosphonium was evaporated in a retort until a considerable quantity of the difficultly soluble amorphous platinum-salt was obtained on addition of dichloride of platinum. The mother-liquor of this salt furnished on evaporation well-formed octohedra.

0·3592 grm. of this platinum-salt gave 0·3447 grm. of carbonic acid and 0·1752 grm. of water.

This result shows that the oxethylated compound had not been changed.

	Vinyl-compound.	Oxethyl-compound.	Experiment.
Carbon	27·41	26·07	26·17
Hydrogen . . .	5·14	5·43	5·42

The temperature in this experiment had never risen above 150° C., which may account for the stability of the oxethylated body under the circumstances.

The vinyl-compound appears to be formed also by the action of heat upon the bromethylated bromide:

$$[(C_2H_4Br)(C_2H_5)_3P]Br = [(C_2H_3)(C_2H_5)_3P]Br + HBr$$

Torrents of hydrobromic acid are evolved, and the residue yields, after treatment with chloride of silver, on addition of dichloride, an octohedral platinum-salt. The decomposition is, however, completed only with difficulty. The evolution of hydrobromic acid continues for hours, even when the salt is kept at a temperature (between 235° and 250°), at which considerable quantities are entirely decomposed. I have thus been prevented from procuring an amount of the salt sufficient for its identification with the vinyl-compound obtained by the action of acetate of silver.

Vinyl-triethylphosphonium-salts are formed in one or two other reactions, which will be noticed in subsequent paragraphs of this inquiry.

SERIES OF DIATOMIC COMPOUNDS. DIPHOSPHONIUM COMPOUNDS.

SALTS OF ETHYLENE-HEXETHYL-DIPHOSPHONIUM.

Dibromide.—The occurrence of this salt among the products of the action of dibromide of ethylene on triethylphosphine has already been mentioned in the introduction to the experimental part of the memoir. On bringing together the materials in the proportions indicated by the equation

$$C_2H_4Br_2 + 2C_6H_{15}P = C_{14}H_{34}P_2Br_2,$$

that is to say, one volume of dibromide of ethylene and three volumes of the phosphorus-base, the diatomic compound is obtained, nearly in the theoretical quantity. It is distinguished from the monatomic product of the same reaction by its much greater solubility even in absolute alcohol, from which it separates, only after almost complete evaporation, in needles which are permanent in the air. In ether this salt is insoluble, as are in fact most of the bromides of the phosphorus-bases, both monatomic and diatomic. The dibromide obtained by the direct action of dibromide of ethylene on triethylphosphine always contains a small quantity of the monatomic bromide, from which it can only be purified with great difficulty. And further, if the dibromide of ethylene has not been carefully purified from adhering hydrobromic acid, the resulting salt is likewise contaminated with traces of the extremely soluble hydrobromate of the phosphorus-base, the presence of which likewise interferes very much with the purification of the product. Lastly, the formation of oxide of triethylphosphine can never be entirely avoided, even when the operation is conducted in an atmosphere of carbonic acid. To obviate these inconveniences, the compound submitted to analysis was prepared by saturating the hydrate, to be presently described, with hydrobromic acid.

I. 0·4837 grm. of bromide gave 0·7091 grm. of carbonic acid and 0·3543 grm. of water.

II. 0·4850 grm. of bromide gave 0·4300 grm. of bromide of silver.

The simplest expression of these results is the formula

$$C_7H_{17}PBr;$$

the formation of the compound, however, and its deportment, fully to be discussed in the following paragraphs, prove unmistakeably that this expression must be doubled, and that the weight and composition of the molecule of this body is represented by the formula

$$C_{14}H_{34}P_2Br_2.$$

	Theory.		Experiment.	
			I.	II.
C_{14}	168	39·62	39·98	——
H_{34}	34	8·02	8·13	——
P_2	62	14·62	——	——
Br_2	160	37·74	——	37·71
	424	100·00		

On comparing the composition of the two bromides which are formed from dibromide of ethylene by the fixation of one or two molecules of triethylphosphine, it could scarcely be doubted that the monatomic compound, even when already formed, must still be in a condition to take up the second molecule of triethylphosphine, and thus to pass into the diatomic bromide. The correctness of this supposition is easily established by experiment. The monatomic bromide acts strongly, even at ordinary temperatures, on a fresh quantity of the phosphorus-base, being transformed, with evolution of heat, into the diatomic compound

$$C_8 H_{19} P Br_2 + C_6 H_{15} P = C_{14} H_{34} P_2 Br_2.$$

In presence of alcohol and at 100°, the reaction is completed in a few seconds. With lively interest have I followed up the result of this simple experiment; for its success obviously pointed to a source from which an almost incalculable number of diatomic compounds of the most varied composition might be obtained. For this reason I have not omitted to establish by numbers the conversion of the monatomic into the diatomic bromide, and in the following sections I shall have frequent occasion to cite analytical results, which leave no doubt as to the facility of this transformation.

The molecular constitution of the new bromide is satisfactorily represented by the formula

$$C_{14} H_{34} P_2 Br_2 = \left[(C_2 H_4)'' \begin{matrix} (C_2 H_5)_3 P \\ (C_2 H_5)_3 P \end{matrix} \right]'' Br_2.$$

The salt is derived from a diatomic metal, a diphosphonium, in which 6 equivs. of hydrogen are replaced by 6 equivs. of ethyl, and the remaining 2 equivs. of hydrogen by the radical ethylene indivisible under the given circumstances. It is the diatomic character of the ethylene that links together the two molecules of triethylphosphine, and gives to the new molecular system the necessary stability.

The dibromide is very easily attacked by silver-compounds, and in this manner an extensive series of very sharply characterized diphosphonium-salts may be obtained, many of which crystallize remarkably well. In these reactions, however, a tendency towards the formation of double compounds is frequently observed, and hence it is for the most part better to prepare the salts by treating the free base with the corresponding acids.

In examining the dibromide, I have made some observations which I may take an opportunity of pursuing further by and by. When the aqueous solution of this salt is mixed with bromine-water, very beautiful yellow needles are immediately separated, consisting of a polybromide. These needles may be recrystallized from boiling water, but, it appears, not without decomposition. They have but an ephemeral stability. On boiling the compound, bromine continues to be evolved, and ultimately the original bromide is left behind. Polybromides, of exactly similar character, are formed by the action of bromine on the bromides of all the ammonium- and phosphonium-bases that I have examined.

I have already pointed out that, in fixing one molecule of triethylphosphine to form

the compound

$$[(C_2H_4Br)(C_2H_5)_3P]Br,$$

dibromide of ethylene exhibits a deportment which might have been expected from bromide of bromethyl, with which it is isomeric. It was of some interest to examine, experimentally, the behaviour of triethylphosphine with monobrominated bromide of ethyl. This substance had never been prepared. I have obtained it, together with the dibrominated bromide of ethyl ($C_2H_3Br_2$)Br, by submitting bromide of ethyl to the action of dry bromine under pressure at a temperature of 180° C. Brominated bromide of ethyl is a heavy aromatic oil, boiling at 110° C., and consequently differing altogether from dibromide of ethylene, which boils at 130° C., and with which it is isomeric. The brominated bromide attacks the phosphorus-base much more slowly than the dibromide; the final result, however, is exactly the same, the bromide of the bromethylated monophosphonium and the dibromide of the ethylene-diphosphonium being produced. The former of these salts is obtained in comparatively small quantity, and I was therefore unable to identify the compound in question with the bromethylated bromide formed by means of the ethylene-compound, otherwise than by the characteristic reaction with silver-salts, mentioned in an earlier paragraph of this paper. The diphosphonium-compound, on the other hand, is easily produced from brominated bromide of ethyl in sufficiently large quantity. I had no difficulty in establishing the absolute identity of this compound with the product obtained from dibromide of ethylene, by a careful comparison of the chemical and physical properties of the substances, and moreover by the analysis of a di-iodide and a platinum-salt prepared by means of the bromide-of-ethyl-derivative. These analyses are given among the analytical details establishing the composition of these salts.

Dihydrate.—The free base is easily obtained by the action of oxide of silver on the dibromide, or better on the di-iodide, which latter is, of all the diphosphonium-compounds of this class, the easiest to obtain in the pure state. If the alcoholic solution of the crude dibromide be used in this experiment, the first portions of oxide of silver added to the liquid are completely dissolved, and the solution, which has already become alkaline, deposits a white crystallized double compound of the dibromide with bromide of silver, which, however, is completely decomposed by further addition of oxide of silver and dilution with water. In this manner there is produced an extremely caustic, nearly odourless liquid, having a strongly alkaline taste, and exhibiting the same bitterness which is so often observed in the analogous bodies of the nitrogen-series. In other respects, the base exhibits the properties which characterize the hydrates of tetrethylphosphonium * and tetrethylammonium †. The solution, when evaporated in an open vessel, rapidly absorbs carbonic acid, and ultimately yields a semi-crystalline mixture of dihydrate and carbonate. When evaporated *in vacuo* over sulphuric acid, the caustic solution gradually dries up to a syrupy, extremely deliquescent mass, which exhibits no traces of crystallization. On mixing the highly concentrated solution of the dihydrate

* Philosophical Transactions, 1857, Part II. p. 583. † Ibid. 1851, Part II. p. 357.

with solution of potassa, the base is separated from the liquid in oily drops, which are, however, readily dissolved on addition of water. The free base, like the corresponding monophosphonium- and even monammonium-compounds, cannot therefore be obtained in a state fit for analysis; its formation, however, as well as its conversion into a series of well-defined salts corresponding to the dibromide, characterize it as an oxide derived from the type,

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2,$$

as the hydrated dioxide of ethylene-hexethyl-diphosphonium:

$$C_{14}H_{36}P_2O_2=\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]''\\H_2\end{matrix}\right\}O_2.$$

Complicated as the construction of this compound must appear, the body is remarkable for its stability. Its solution may be boiled and considerably concentrated upon the water-bath without decomposition, and remains unchanged even when exposed for some time under pressure to a temperature of 150°; indeed the decomposition of the hydrate does not begin till the liquid is evaporated to dryness. The changes which this compound suffers under the influence of higher temperatures are not without interest. They are rather intricate, and I propose therefore to devote a special paragraph to their study.

In its deportment with metallic salts, the hydrate of the diphosphonium closely resembles the fixed alkalies, as may be seen from the following Table:—

Deportment of the Hydrate of the Diphosphonium with reagents.

Barium-salts Strontium-salts Calcium-salts Magnesium-salts	White precipitates of the hydrates.
Aluminium-salts	White precipitate of hydrate of aluminium, soluble in excess of the precipitant.
Chromium-salts	Green precipitate of hydrate of chromium, soluble in an excess of the precipitant, and reprecipitated on ebullition.
Nickel-salts	Apple-green precipitate of the hydrate.
Cobalt-salts	Blue precipitate of the hydrate.
Iron-salts:—	
Ferrosum	Greenish precipitate of the hydrate.
Ferricum	Reddish-brown precipitate of the hydrate.
Zinc-salts	White gelatinous precipitate of the hydrate, insoluble in excess.
Lead-salts	White amorphous precipitate of hydrate of lead, soluble in excess.
Silver-salts	Black-brown precipitate of oxide of silver.
Mercury-salts:—	
Mercurosum	Black precipitate of the suboxide.
Mercuricum	Yellow precipitate of the oxide.

Copper-salts . .	Light blue precipitate of the hydrate, insoluble in excess: in presence of sugar, the precipitate dissolves in excess, forming an azure-blue solution, from which, if glucose has been employed, a red precipitate of suboxide of copper separates on ebullition.
Cadmium-salts Bismuth-salts	White precipitates of the hydrates.
Tin-salts:—	
Stannosum:—	
Chloride, containing free hydrochloric acid	White acicular precipitate of a double compound.
Stannicum:—	
Chloride . .	White gelatinous precipitate, extremely soluble in excess.
Antimony-salts:—	
Trichloride . .	White acicular precipitate of a double compound.
Gold-salts:—	
Trichloride .	Golden-yellow crystalline precipitate of a double compound.
Platinum-salts:—	
Dichloride . .	Pale-yellow, slightly crystalline precipitate of a double compound.

These are, with few exceptions, the reactions of a solution of potassa. It is scarcely necessary to add that the hydrate of the diphosphonium expels, even at the common temperature, ammonia, phenylamine, triethylphosphine, and a considerable number of other amines and phosphines from their saline combinations.

The free base exhibits the deportment of caustic potassa also towards iodine and sulphur. It dissolves crystals of *iodine* with facility; the colourless solution is neutral, and yields on evaporation a syrup-like half-crystalline mass, easily recognized as a mixture of the di-iodide with the di-iodate. Treatment with alcohol separates the crystals of the more difficultly soluble iodide from the gummy iodate. On adding concentrated hydrochloric acid to the liquid obtained by dissolving iodine in the free base, a dark-coloured substance (iodine or a periodide) is separated; after a few seconds, however, the liquid is decolorized and solidifies to a mass of beautiful lemon-yellow crystals. The diphosphonium-salts are thus seen to exhibit phenomena exactly similar to those which were observed by Weltzien in the case of the compounds of tetramethyl- and tetrethyl-ammonium. I hope to find an opportunity of returning to a more minute examination of the yellow compound, which, by recrystallization from boiling alcohol, may be obtained in splendid needles, and which will probably be found to be a compound of the di-iodide with chloride of iodine. For the present I may remark that similar compounds are formed by all the bases of the type ammonium and diammonium which I have examined, provided they belong to that class in which the substitution is

complete. A variety of monophosphonium- and monarsonium-salts, and lastly of compounds of phosphammoniums and phospharsoniums, submitted to the same process, have furnished perfectly similar results. Hydrochloric acid occasionally produces crystalline precipitates in the concentrated solutions of the iodates, even of bases containing unreplaced hydrogen; these precipitates disappear, however, on addition of water, or on gently warming, and are essentially different from the compounds previously mentioned. *Sulphur* dissolves in a concentrated solution of the dihydrate, although with difficulty, to a yellow liquid, which precipitates the black sulphide from lead-solutions, and is decomposed by acids, with separation of sulphur and evolution of sulphuretted hydrogen. *Phosphorus* is not attacked by the solution of the hydrate, not a trace of phosphoretted hydrogen being evolved even by protracted ebullition.

Disulphhydrate.—The solution of the base saturated with hydrosulphuric acid, when allowed to remain for some time over sulphuric acid *in vacuo*, dries up to a gummy mass, which exhibits as little inclination to crystallize as the dihydrate itself. When evaporated on the water-bath in contact with the air, the disulphhydrate is decomposed, the sulphur being oxidized; ultimately an imperfect crystallization of the sulphate remains behind.

Dichloride.—This salt is easily obtained by treating the dibromide or the di-iodide with chloride of silver, and also by saturating the free base with hydrochloric acid; it is extremely soluble in water and in alcohol, insoluble in ether. The concentrated solution solidifies over sulphuric acid into a mass of large and highly deliquescent crystalline plates of a pearly lustre, which may be exposed to a very high temperature (290° to 300°) without the slightest alteration. The salt is precipitated unchanged from its aqueous solution by potassa. For analysis, the salt was dried *in vacuo* over sulphuric acid.

0·4325 grm. of dichloride gave 0·3670 grm. of chloride of silver.

The chloride accordingly contains

$$C_{14}H_{34}P_2Cl_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2.$$

	Theory.		Experiment.
1 equiv. of Diphosphonium .	264	78·81	——
2 equivs. of Chlorine . . .	71	21·19	20·99
1 equiv. of Dichloride . . .	335	100·00	

The dichloride forms with metallic chlorides numerous well-crystallized double compounds, some of which will be more particularly described hereafter.

The dichloride of the ethylene-diphosphonium is likewise produced by the action of monochlorinated chloride of ethyl, prepared in accordance with REGNAULT'S indications, by the action of chlorine upon chloride of ethyl. The chlorinated compound acts but slowly upon triethylphosphine at 100° C. By digesting the mixture for twenty-four hours at 120°, a considerable proportion solidified to a white fibrous crystalline mass, which

proved to be exclusively the dichloride of the diphosphonium. It was identified by conversion into the characteristic platinum-salt, and subsequently into the iodide, both of which were analysed. The details are given under the head of the di-iodide and platinum-salt of the diphosphonium.

Di-iodide.—This salt is perhaps the most characteristic of the diphosphonium-compounds. Crystallizing with peculiar readiness,—being easily soluble in hot, but sparingly soluble in cold water,—slightly soluble also in alcohol, and insoluble in ether,—it possesses all the properties which can facilitate the preparation of a pure and definite substance. It has therefore, for the most part, served as the starting-point of the diphosphonium-compounds.

I have already remarked that, in the preparation of the monatomic bromide, the formation of the dibromide can scarcely ever be entirely prevented. The mother-liquors, remaining after numerous preparations of the monatomic bromide, were therefore united and treated with oxide of silver, whereby a caustic liquid was obtained containing the hydrate of the diphosphonium, contaminated with the hydrate of the oxethylated monophosphonium arising from the decomposition of the bromethylated compound. These hydrates were converted, by saturation with hydriodic acid, into the corresponding iodides, the separation of which presented no further difficulty, inasmuch as the iodide of the oxethylated monophosphonium is extremely soluble in water and in alcohol. The sparingly soluble di-iodide was easily obtained in a state of perfect purity by several crystallizations. The crystals are anhydrous. Any hygroscopic moisture that may adhere to them is most conveniently removed by drying them over sulphuric acid, since the salt begins to turn slightly brown at 100°.

I. 0·5690 grm. of iodide gave 0·6742 grm. of carbonic acid and 0·3403 grm. of water.
II. 0·2270 grm. of iodide gave 0·2055 grm. of iodide of silver.
III. 0·3245 grm. of iodide gave 0·2935 grm. of iodide of silver.

The salt which served for analysis III. had been prepared from a dibromide obtained by submitting the pure bromide of the bromethylated triethylphosphonium to the action of triethylphosphine.

IV. 0·3970 grm. of iodide gave 0·3607 grm. of iodide of silver. The salt used for this determination had been prepared by submitting triethylphosphine to the action of *bromethylated bromide of ethyl* (see the paragraph on the dibromide of ethylene-diphosphonium), converting the dibromide formed into the corresponding chloride, into the platinum-salt, and ultimately into the iodide.

V. 0·4090 grm. of iodide gave 0·3700 grm. of iodide of silver. The specimen used for analysis had been prepared by treating triethylphosphine with *chlorinated chloride of ethyl*, precipitation of the product of the reaction as platinum-salt, and transformation of the latter into the iodide.

The formula

$$C_{14}H_{34}P_2I_2=\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2$$

requires

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
C_{14}	168	32·43	32·31	——	——	——	——
H_{34}	34	6·57	6·64	——	——	——	——
P_2	62	11·97	——	——	——	——	——
I_2	254	49·03	——	48·92	48·88	49·10	48·88
	518	100·00					

The di-iodide crystallizes from boiling water in needle-shaped crystals, which often attain a considerable size. Quintino Sella has communicated to me the following results, which he has obtained on examining these crystals:—

"System trimetric:—

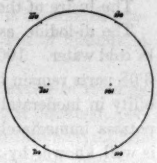
001, 101=45° 9′

100, 110=60° 18′.

Forms observed:—

110, 101 (Fig. 41).

Fig. 41.



Angles.	Calculated.	Observed.
110, $\bar{1}$10 =	59° 24′	59° 22′
101, $\bar{1}$01 =	90 18	90 16
110, 101 =	69 26	69 21

According to Naumann:—

$a:b:c=1·0052:1:0·5704$.

Forms observed:—

∞P, $\breve{\text{P}}\infty$.

According to Weiss:—

$a:b:c=1:0·5704:1·0052$.

Forms observed:—

$a:b:\infty c$; $a:\infty b:c$.

According to Levy:—

M M=120° 36′; $b:h=1:0·8732$.

Forms observed:—

M, e'.

Combinations observed:—

110, 101 (Figs. 42, 43).

110, 101 with other faces, too much rounded to admit of correct determination (Fig. 44).

Fig. 42.

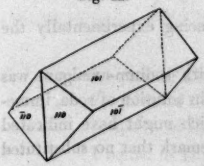


Fig. 43.

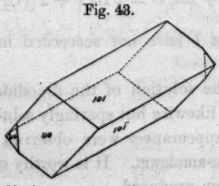
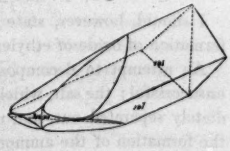


Fig. 44.



Cleavages 110 and 101 distinct and easily obtained.

The crystals are long needles; the faces $\bar{1}\,1\,0$ are often but little developed (Fig. 43); the crystals have then a monoclinic aspect; but the measurement of the angles $1\,1\,0$, $1\,0\,1$ and $\bar{1}\,1\,0$, $\bar{1}\,0\,1$ has furnished nearly the same result; and moreover, on examining the crystals with the polarizing microscope, the line $[0\,1\,0]$ is found to be nearly one of the axes of elasticity.

The angle $1\,0\,1$, $\bar{1}\,0\,1$ is so near to 90°, that there might appear some reason for regarding the crystals as dimetric hemihedrals. I am not, however, of this opinion, for I have observed only two cleavages, $1\,1\,0$, $\bar{1}\,1\,0$, instead of the four corresponding to the dimetric system; moreover the angle $1\,0\,1$, $\bar{1}\,0\,1$ has *always* been found a little greater than 90°.

The needles, when small, are transparent; the larger ones are rather milky, and hollow inside.

The lustre of the faces $1\,0\,1$ is slightly nacreous; that of the faces $1\,1\,0$ is vitreous."

The di-iodide, as already observed, is very much more soluble in boiling water than in cold water. 100 parts of boiling water dissolve 458·3 parts of the salt, of which only 3·08 parts remain in solution at 12°. A remarkable character of the salt is its insolubility in moderately concentrated solution of potassa; the dilute solution mixed with potassa immediately yields a crystalline precipitate; the same property is exhibited, as is well known, by the iodides of tetrethylammonium and of the other ammonium- and phosphonium-metals. The solution of the di-iodide, like those of the diphosphonium-salts in general, is perfectly neutral; it is colourless when first prepared, but on exposure to light, soon acquires a tint of yellow, and finally turns brown; at the same time depositing a reddish compound, doubtless analogous to the periodides, which, as I observed some time ago, are formed under similar circumstances from the iodides of tetramethyl- and tetrethyl-ammonium, and which have since been so successfully studied by Weltzien. This red compound is immediately precipitated on adding a solution of iodine to the colourless solution. The di-iodide, like most diphosphonium-compounds, exhibits great stability. It melts, without the slightest decomposition, at 231°, and solidifies, with crystalline structure, a few degrees lower. When more strongly heated over an open flame, it is decomposed, with formation of a red-brown substance, which I have not examined. On distilling the di-iodide with excess of caustic baryta in an atmosphere of hydrogen, triethylphosphine passes over; no gaseous product is formed in this reaction. Together with iodide of barium which remains behind, and triethylphosphine which distils over, oxide of ethylene is probably formed in this reaction.

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2 + Ba_2O = 2\,BaI + 2\,[(C_2H_5)_3P] + (C_2H_4)''O.$$

I should, however, state that I have not succeeded in tracing experimentally the formation of oxide of ethylene.

An attempt to decompose the solution of the di-iodide with sodium-amalgam was unsuccessful; the salt, which is likewise but sparingly soluble in solution of soda, immediately separated out, and no appearances were observed which might have indicated the formation of the ammonium-amalgam. It is worthy of remark that no substituted ammonium-amalgam has yet been produced.

The di-iodide forms, with various metallic salts, crystalline double compounds, among which I have more particularly examined the zinc-salt; its analysis will be given further on.

Difluoride.—The solution of the hydrate, neutralized with hydrofluoric acid and dried over sulphuric acid, leaves a colourless transparent syrup, which does not crystallize, even after standing for a considerable length of time in air or *in vacuo*. The fluorine-compound, like the other diphosphonium-salts, is soluble in alcohol but insoluble in ether.

Silico-fluoride.—The solution, neutralized with hydrofluosilicic acid, likewise failed to yield crystals by evaporation.

Dicyanide.—The solution of the hydrate, mixed with excess of hydrocyanic acid, retains its alkaline reaction; when evaporated on the water-bath, it gives off every trace of hydrocyanic acid. On digesting a solution of the di-iodide with excess of cyanide of silver, a double compound dissolves, which crystallizes in splendid needles, but is likewise decomposed by evaporation, with evolution of hydrocyanic acid and separation of cyanide of silver.

Disulphocyanate.—When a solution of the di-iodide is boiled with excess of recently precipitated sulphocyanate of silver, a solution of the disulphocyanate is obtained, perfectly free from silver, and solidifying by evaporation on the water-bath into a crystalline mass. The salt dissolves readily in water and in alcohol, and is precipitated therefrom by ether. The aqueous solution is likewise precipitated by potassa, the oily drops thus separated gradually solidifying into crystalline rosettes.

Dinitrate.—This salt, prepared by saturating the base with nitric acid, forms laminar crystals, permanent in the air, extremely soluble in water, less soluble in alcohol, and precipitated from the alcoholic solution by ether, as an oil which gradually solidifies. The solution forms with mercuric chloride a precipitate which crystallizes in needles.

Diperchlorate.—This salt is perhaps the most beautiful of the diphosphonium-compounds. On mixing moderately concentrated solutions of the hydrate and perchloric acid, the liquid is soon traversed by delicate crystalline needles, often an inch long. They may be recrystallized from boiling water and dried at 100° without decomposition. At a higher temperature, they are decomposed, with slight detonation.

In the analysis of the perchlorate, the diphosphonium was weighed in the form of the nearly insoluble platinum-salt.

0·3130 grm. of diperchlorate, evaporated to dryness with an excess of dichloride of platinum, gave, after treatment with alcohol, 0·4535 grm. of the diphosphonium-platinum-salt.

$$C_{14}H_{34}P_2Cl_2O_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2O_8.$$

		Theory.	Experiment.
1 equiv. of Diphosphonium . .	264	57·02	56·71
2 equivs. of Chlorine . . .	71	15·33	——
8 equivs. of Oxygen	128	27·65	——
1 equiv. of Diperchlorate. . .	463	100·00	

Di-iodate.—The base, neutralized with iodic acid and evaporated over sulphuric acid, yields an extremely deliquescent syrup which crystallizes but gradually. Solution of potassa separates the hydrate from the concentrated solution, in oily drops, sparingly soluble crystalline iodate of potassium being at the same time precipitated. The solution, mixed with hydrochloric acid, yields the lemon-yellow crystalline compound already mentioned.

Carbonate.—The solution of the oxide remains alkaline, even after saturation with carbonic acid; on evaporation, it leaves a mass having a slightly crystalline structure.

Sulphate.—Radio-crystalline, extremely deliquescent salt. Repeated attempts to produce diphosphonium-alums by mixing the solution with the sulphates of aluminium and chromium were unsuccessful.

Chromate.—The solution of the free base, neutralized with pure chromic acid, deposits, when in an atmosphere dried by sulphuric acid, extremely soluble needles arranged in stellated groups. With excess of chromic acid, nothing but an uncrystallizable syrup is obtained.

Oxalate.—Both the acid and the neutral solution of the base in oxalic acid dries up to a slightly crystalline mass.

Phosphate.—The di-iodide, boiled with excess of phosphate of silver, yields a neutral solution of the phosphate of the diphosphonium, which remains as a slightly crystalline mass when the solution is evaporated. Crystallization is not promoted by addition either of free phosphoric acid or of the hydrate.

Tartrate.—Extremely soluble; difficult to crystallize.

Dipicrate.—The aqueous solution of picric acid, added to a moderately concentrated solution of the hydrate, instantly produces a yellow crystalline precipitate, which separates from the boiling alkaline solution in long needles.

The diphosphonium-salts form a long series of double compounds, most of which crystallize splendidly.

Platinum-salt.—The solution of the dichloride, even when extremely dilute, yields with dichloride of platinum a pale-yellow precipitate, which appears amorphous to ordinary observation, but when examined under a microscope of rather high power, resolves itself into small prisms. This salt is nearly insoluble in cold and even in boiling water, so that, as already observed, the diphosphonium may be quantitatively estimated in this form. The precipitate dissolves, though with difficulty, in concentrated hydrochloric acid, and crystallizes from the solution, by slow cooling, in small but well-defined crystals of a bright orange-red colour.

Quintino Sella has examined these crystals, and obtained the following results:—

"System monoclinic:—

100, 001=82° 36′.

Forms observed:—

100, 010, 001 (Fig. 45).

Fig. 45.

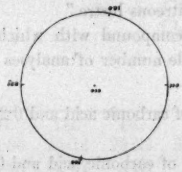
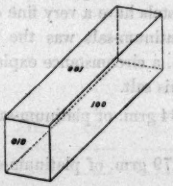


Fig. 46.



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Angles.	Calculated.	Observed.
100, 010 =	90° 0′	90° 3′
100, 001 =	82 36	82 36
010, 001 =	90 0	89 57

According to Naumann:—

$\gamma = 82° 36'$.

Forms observed:—

$\infty P \infty$, $\infty P \infty$, 0 P.

According to Weiss:—

$a : c = 97° 24'$.

Forms observed:—

$a : \infty b : \infty c$; $\infty a : b : \infty c$; $\infty a : \infty b : c$.

According to Levy:—

$h' P = 97° 24'$.

Forms observed:—

h', g', P.

Combinations observed:—

100, 010, 001 (Fig. 46).

Cleavages 100, 010, 001 distinct and easily obtained, more especially 010.

The crystals are elongated in the direction of the axis of symmetry, and often hollowed out for a great part of their length when rather thick, that is to say, when their sides attain the width of half a millimetre. The hollow has the form of a pyramid having its base on the face 010 and its apex towards the centre of the crystal. The face 010 is often reduced to a very narrow rectangular rim. The opposite apex of the crystal is irregular, as if it had adhered to the side of the vessel. The face 001 is in general rather more developed than 100.

The crystals are optically negative. The plane of the optical axes is parallel to the line of symmetry [010]; the principal medium-line is perpendicular to the latter, and

forms an angle of about 30° with a line normal on face 0 0 1. In fact, a plate parallel to 0 1 0 stops the passage of a ray of polarized light in that direction. Moreover, rings are observed through the faces 0 0 1, and in a plane parallel to the line of symmetry 0 1 0, and rather inclined towards a line normal on such face. The angle of the optical axes, seen in this manner through the faces 0 0 1, appears to be very nearly 110°.

The crystals have a very fine orange-colour and a vitreous lustre."

This platinum-salt was the first diphosphonium-compound with which I became acquainted, a circumstance explaining the considerable number of analyses which were made of this salt.

I. 0·6534 grm. of platinum-salt gave 0·5938 grm. of carbonic acid and 0·2995 grm. of water.

II. 0·7179 grm. of platinum-salt gave 0·6545 grm. of carbonic acid and 0·3135 grm. of water.

III. 0·3568 grm. of platinum-salt gave 0·3289 grm. of carbonic acid and 0·1585 grm. of water.

IV. 0·3250 grm. of platinum-salt gave 0·3009 grm. of carbonic acid and 0·1480 grm. of water.

V. 0·5809 grm. of platinum-salt gave 0·5228 grm. of carbonic acid and 0·2670 grm. of water. This compound had been prepared from a diphosphonium-salt obtained by the action of brominated bromide of ethyl upon triethylphosphine.

VI. 0·7200 grm. of platinum-salt, when fused with carbonate of sodium, gave 0·2120 grm. of platinum and 0·9120 grm. of chloride of silver.

VII. 0·4075 grm. of platinum-salt gave 0·1205 grm. of platinum and 0·5235 grm. of chloride of silver.

VIII. 0·3470 grm. of platinum-salt gave 0·1030 grm. of platinum and 0·4428 grm. of chloride of silver.

IX. 0·4615 grm. of platinum-salt gave 0·1355 grm. of platinum.

X. 0·4105 grm. of platinum-salt gave 0·1210 grm. of platinum. This salt had been obtained by the action of chlorinated chloride of ethyl upon triethylphosphine. The mother-liquor furnished by the analysis of the iodide (V.) had served for its preparation.

XI. 0·6158 grm. of platinum-salt gave 0·7778 grm. of chloride of silver.

These numbers fix the formula

$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2,$$

the theoretical values of which I place in juxtaposition with the experimental percentages:

	Theory.	
C_{14}	168	24·91
H_{34}	34	5·05
P_2	62	9·19
Pt_2	197·4	29·27
Cl_6	213	31·58
	674·4	100·00

Experiment.										
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
24·78	24·86	25·14	25·25	24·54	——	——	——	——	——	——
5·09	4·85	4·94	5·06	5·10	——	——	——	——	——	——
——	——	——	——	——	——	——	——	——	——	——
——	——	——	——	——	29·44	29·57	29·68	29·36	29·11	——
——	——	——	——	——	31·33	31·78	31·57	——	——	31·24

Palladium-salt.—A dilute solution of the dichloride is not precipitated by chloride of palladium. On concentrating the mixture and allowing it to cool slowly, reddish-yellow prisms make their appearance: by rapid evaporation a brick-red crystalline powder is obtained. Alcohol added to the aqueous solution of the two salts throws down the double salt as a chocolate-coloured crystalline magma composed of small interlaced needles. I have not analysed this compound.

Gold-salt.—Beautiful golden-yellow needles, difficultly soluble in cold, easily soluble in boiling water, and containing

$$C_{14}H_{34}P_2Au_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2AuCl_3,$$

as shown by the following analyses:—

I. 0·6200 grm. of gold-salt gave 0·4159 grm. of carbonic acid and 0·2032 grm. of water.

II. 0·3540 grm. of gold-salt gave 0·1490 grm. of gold.

	Theory.		Experiment.	
			I.	II.
C_{14}	168	17·83	18·29	——
H_{34}	34	3·61	3·64	——
P_2	62	6·58	——	——
Au_2	394	41·83	——	42·09
Cl_8	284	30·15	——	——
	942	100·00		

Mercury-salt.—Delicate crystalline needles or laminæ, sparingly soluble in water and in alcohol, obtained by mixing the chloride of the diphosphonium with mercuric chloride.

I. 0·2660 grm. of mercury-salt gave 0·2390 grm. of the diphosphonium-platinum-salt and 0·1255 grm. of sulphide of mercury.

II. 0·5650 grm. of mercury-salt gave 0·2670 grm. of sulphide of mercury and 0·5515 grm. of chloride of silver.

These analyses lead to the formula

$$C_{14}H_{34}P_2Hg_3Cl_5 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 3\,HgCl,$$

as seen from the following comparison:—

	Theory.		Experiment.	
			I.	II.
1 equiv. of Diphosphonium .	264·0	35·60	35·18	——
3 equivs. of Mercury . . .	300·0	40·46	40·64	40·73
5 equivs. of Chlorine . . .	177·5	23·94	——	24·14
1 equiv. of Mercury-salt . .	741·5	100·00		

Tin-salt.—This salt, which is prepared like the mercury-compound, crystallizes from water in large well-formed prismatic crystals. According to some determinations, which, however, gave only approximate results, the tin-salt appears to have the composition

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 4\,SnCl.$$

Di-iodide and Iodide of Zinc.—On mixing the two solutions, a crystalline precipitate is obtained, which separates in long needles when recrystallized from boiling water. The salt, which is apt to assume a yellowish coloration, contains

$$C_{14}H_{34}P_2Zn_2I_4 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2,\ 2\,ZnI.$$

0·5735 grm. of zinc-salt gave 0·6401 grm. of iodide of silver.

The above formula requires the following values:—

	Theory.		Experiment.
1 equiv. of Diphosphonium . .	264	31·54	——
2 equivs. of Zinc	65	7·77	——
4 equivs. of Iodine	508	60·69	60·31
1 equiv. of Zinc-salt	837	100·00	

Dibromide and Bromide of Silver.—I have mentioned this salt already when describing the preparation of the hydrate from the dibromide. When oxide of silver, which should not be mixed with too much water, is added in small portions to a boiling concentrated solution of the dibromide in alcohol as long as it dissolves, the filtered solution deposits on cooling white crystals, which contain

$$C_{14}H_{34}P_2AgBr_3 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2,\ AgBr.$$

Analysis has furnished the following numbers:—

I. 0·4465 grm. of double salt, fused with carbonate of sodium, left, after removal of the bromide of sodium, a silver-residue, which, when treated with nitric and hydrochloric acid, gave 0·1042 grm. of chloride of silver.

II. 0·6442 grm. of double salt gave, on boiling with water, a residue of 0·2710 grm. of bromide of silver; the filtrate yielded with nitrate of silver an additional amount of 0·3220 grm. of bromide of silver; the total amount of bromide of silver obtained being therefore 0·5930 grm.

III. 0·7065 grm. of double salt gave by treatment with nitrate of silver 0·6538 grm. of bromide of silver.

	Theory.		Experiment.		
			I.	II.	III.
C_{14}	168	27·45	——	——	——
H_{34}	34	5·56	——	——	——
P_2	62	10·13	——	——	——
Ag	108	17·65	17·56	——	——
Br_3	240	39·21	——	39·17	39·37
	612	100·00			

The salt crystallizes, but not readily, from boiling alcohol. It is immediately decomposed by water, bromide of silver being separated, and the bromide of the diphosphonium passing into the solution.

In describing the general character of the action of dibromide of ethylene upon triethylphosphine, I have mentioned that, in addition to the monatomic and diatomic bromides, which are the principal products of the reaction, secondary compounds may be formed, but always in comparatively small quantities. The mother-liquors generally contain oxide of triethylphosphine, formed by the action of the atmosphere; they contain, moreover, bromide of triethylphosphonium, if the dibromide had not been carefully deprived of hydrobromic acid. The bromide of triethylphosphonium, however, under certain conditions, arises from the scission of dibromide of ethylene into hydrobromic acid and bromide of vinyl, the latter producing in this case the bromide of vinyltriethylphosphonium. I had an opportunity of establishing this fact experimentally, when preparing a considerable quantity of the dibromide of the diphosphonium. The phosphorus-base having been employed in excess in this operation, not a trace of the bromethylated monophosphonium had been formed, the absence of which was carefully proved by a special experiment. The bromides were then transformed into chlorides and the latter precipitated by dichloride of platinum; the mother-liquor filtered off from the copious precipitate of the diphosphonium-salt was considerably evaporated, when, on cooling, well-formed octohedra were deposited, which were recrystallized from water.

0·4835 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1365 grm. = 28·23 per cent. of platinum.

The theoretical platinum percentage of the compound

$$[(C_2H_3)(C_2H_5)_3P]Cl, PtCl_2$$

is 28·19. The formation of the vinyl-compound under these circumstances is easily explained.

$$C_2H_4Br_2 + 2[(C_2H_5)_3P] = [(C_2H_3)(C_2H_5)_3P]Br + [(C_2H_5)_3HP]Br.$$

The amount of vinyl-compound produced is but very small in proportion to that of the other salts which are formed in the mutual action between triethylphosphine and dibromide of ethylene.

Action of Heat upon the Hydrate of the Diphosphonium.

The hydrate, when submitted to the action of heat, undergoes a series of remarkable changes, which I have studied with lively interest. The decomposition commences at 160°; on raising the temperature gradually to 250°, the whole of the hydrate passes over in the form of liquid and gaseous products. The liquid product consists of triethylphosphine and oxide of triethylphosphine; the gas contains a considerable proportion of ethylene, which is readily characterized by its deportment with bromine. This transformation may be represented by the following equation:—

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3P + (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The succession of changes, however, through which the hydrate runs before it is broken up, shows unmistakeably that this equation can represent but one phase, even of the final transformation of the diphosphonium-compound. The study of the intermediate changes presents unusual difficulties, and I confess at once that I have failed to solve the problem to my entire satisfaction.

The experiments performed with a view of disentangling the intricacies of these reactions, will perhaps be better understood if I commence with setting forth the ideas which I have ultimately formed of these metamorphoses, and then state the analytical results which have assisted me in forming them.

Under the influence of heat, the hydrate of the diphosphonium undergoes two principal transformations, which are accomplished side by side. A portion of this compound gives rise to the formation of oxide of triethylphosphine and hydrate of tetrethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3PO + \left.\begin{matrix}[(C_2H_5)_4P] \\ H\end{matrix}\right\}O,$$

the latter splitting ultimately into oxide of triethylphosphine and hydride of ethyl,

$$\left.\begin{matrix}[(C_2H_5)_4P] \\ H\end{matrix}\right\}O = (C_2H_5)_3PO + (C_2H_5)H;$$

a second portion is resolved into triethylphosphine and hydrate of oxethyl-triethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3P + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O;$$

the latter may undergo, at a high temperature, a further transformation, separating, partially at least, into water and hydrate of vinyl-triethylphosphonium,

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\H\end{matrix}\right\}O,$$

the vinyl-compound yielding, in the last stage of the reaction, oxide of triethylphosphine and ethylene,

$$\left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\H\end{matrix}\right\}O = (C_2H_5)_3PO + C_2H_4.$$

The separation of the triethylphosphine and its oxide by the action of heat upon the hydrated diphosphonium requires no special experimental demonstration. To individualize the other compounds, the following experiments were made:—A considerable quantity of the dihydrate was evaporated in a retort in an atmosphere of hydrogen. As soon as the phosphorus-base began to distil freely—at about 190° C.—the operation was interrupted, and the residuary alkaline liquid saturated with hydrochloric acid and precipitated with dichloride of platinum. A dingy yellow amorphous precipitate was thrown down, insoluble in cold water, and the mother-liquor, on evaporation, furnished a mass of deep orange-red octohedra, which were transformed into the corresponding iodine-compound. The salt thus obtained proved unmistakeably a mixture of two compounds of different solubility. The less soluble was obtained in beautiful crystals, exhibiting all the characters of iodide of tetrethylphosphonium. The salt was identified by analysis.

I. 0·7480 grm. of iodide gave 0·6360 grm. of iodide of silver.

II. 0·3215 grm. of iodide, once more recrystallized, gave 0·2760 grm. of iodide of silver.

	Theory of the iodide of			Experiment.	
	Oxethylated triethyl-phosphonium.	Vinyl-triethyl-phosphonium.	Tetrethyl-phosphonium.	I.	II.
Iodine . .	43·80	46·69	46·35	45·94	46·38

The platinum-salt corresponding to the difficultly soluble iodide gave, on analysis, the following results:—

I. 0·4727 grm. of platinum-salt gave 0·4723 grm. of carbonic acid and 0·2470 grm. of water.

II. 0·4478 grm. of platinum-salt gave 0·4442 grm. of carbonic acid and 0·2305 grm. of water.

III. 0·5430 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1510 grm. of platinum.

IV. 0·4097 grm. of platinum-salt gave 0·1145 grm. of platinum.

V. 0·6140 grm. of platinum-salt gave 0·1728 grm. of platinum.

I place the percentages deduced from these analyses in juxtaposition with the theoretical values corresponding to the platinum-salts of vinyl-triethyl- and tetrethyl-phosphonium.

	Theory.		Experiment.				
	Vinyl-compound.	Tetrethyl-compound.	I.	II.	III.	IV.	V.
Carbon . .	27·41	27·26	27·25	27·05	——	——	——
Hydrogen . .	5·14	5·68	5·80	5·71	——	——	——
Platinum . .	28·19	28·02	——	——	27·81	27·94	28·14

The hydrogen-determinations prove unequivocally that the compound is the platinum-salt of the tetrethylphosphonium. The formation of the tetrethylphosphonium-compound is moreover demonstrated by the analysis of the corresponding gold-salt.

I. 0·5783 grm. of gold-salt gave 0·4158 grm. of carbonic acid and 0·2200 grm. of water.

II. 0·5795 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0·2352 grm. of gold.

	Theory.		Experiment.	
	Vinyl-triethyl-phosphonium-salt.	Tetrethyl-phosphonium-salt.	I.	II.
Carbon . .	19·83	19·75	19·61	——
Hydrogen . .	3·71	4·11	4·22	——
Gold . . .	40·70	40·53	——	40·59

Here likewise the hydrogen-determination is characteristic of the tetrethylphosphonium-compound. The result of analysis is most satisfactorily confirmed by the crystallographical examination of the salts under consideration. Q. Sella has compared the crystals of the iodide above-mentioned with crystals of iodide of tetrethylphosphonium obtained in the usual way. I have appended at the conclusion of this paper the elaborate investigation of this beautiful salt, with which my friend has furnished me.

Far less conclusive is the experimental evidence which I am enabled to offer in support of the opinion, that the hydrate of tetrethylphosphonium formed by the action of heat on the hydrated diphosphonium is accompanied by the oxethylated triethylphosphonium-compound. The principal argument in favour of this view is the abundant evolution of triethylphosphine, which cannot be understood unless we assume the simultaneous formation of the oxethylated, or the vinyl-compound. I have failed in my endeavours to prepare the more soluble iodide which accompanies the tetrethylphosphonium-compound in a state of purity. Nor was the attempt to separate the two compounds in the form of platinum-salts rewarded by better success. Both platinum-salts crystallize in octohedra which differ but slightly in solubility. Nevertheless the following determinations leave but little doubt as to the presence of the oxethylated phosphonium among the products resulting from the decomposition of the hydrate of diphosphonium under the influence of heat.

I. 0·320 grm. of platinum-salt gave 0·3091 grm. of carbonic acid and 0·1625 grm. of water.

II. 0·4675 grm. of platinum-salt gave 0·4573 grm. of carbonic acid and 0·2352 grm. of water.

III. 0·3250 grm. of platinum-salt of the same preparation, treated with sulphuretted hydrogen, &c., gave 0·0890 grm. of platinum.

	Theory.		Experiment.		
	Tetrethylphosphonium-salt.	Oxethyl-triethylphosphonium-salt.	I.	II.	III.
Carbon . .	27·26	26·07	26·34	26·67	——
Hydrogen .	5·68	5·43	5·64	5·59	——
Platinum . .	28·02	26·81	——	——	27·38

The experimental numbers characterize a mechanical mixture of the two platinum-salts.

The action of heat upon the hydrate of the diphosphonium induces yet another transformation, to which I have already alluded when mentioning the dingy yellow insoluble precipitate which is formed on addition of dichloride of platinum to the product of the action of heat upon the hydrate, neutralized with hydrochloric acid.

The following paragraph contains the fragmentary information which I have collected in studying these changes.

PARADIPHOSPHONIUM-COMPOUNDS.

The basic compound which yields the amorphous yellow platinum-salt repeatedly mentioned, is a transient product of the action of heat on the hydrated diphosphonium. If during distillation, the alkaline residue in the retort be tested from time to time with dichloride of platinum, a point is soon reached, when instead of the slightly crystalline precipitate, perfectly insoluble in dilute hydrochloric acid, which appears at the commencement of the operation, an amorphous, generally dingy yellow precipitate is obtained, immediately dissolving on addition of a few drops of dilute hydrochloric acid. If the distillation be now interrupted and the residue neutralized with hydrochloric acid, and mixed with a few drops of dichloride of platinum, a discoloured precipitate is thrown down, the filtrate from which, on addition of a further quantity of platinum-solution, yields the amorphous salt, of a light yellow colour, and in a state of purity. This salt exhibits no trace of crystalline structure, even when examined under the most powerful microscope: in the perfectly dry state it is remarkably electrical, flying about in all directions during trituration.

The same substance is obtained when the hydrated oxethyl-triethylphosphonium is submitted to the action of heat. By interrupting the process at a convenient time, and adding dichloride of platinum to the neutralized residue, phenomena identical with those just mentioned are observed.

The compound which produces the amorphous yellow precipitate was lastly obtained, under the following circumstances.

While engaged with the study of the vinyl-compounds, the examination of which I

have described in one of the previous paragraphs of this paper, the idea suggested itself that the bromide of vinyl-triethylphosphonium might also be formed by the action of bromide of vinyl (C_2H_3Br) on triethylphosphine:

$$(C_2H_5)_3P + C_2H_3Br = [(C_2H_3)(C_2H_5)_3P]Br.$$

In performing the experiment, I had an opportunity of observing the sluggishness of action of this bromide, often previously noticed in experimenting in the ammonium-series. When gaseous bromide of vinyl is passed through triethylphosphine, not a trace of it is fixed by the phosphorus-base. Triethylphosphine may be distilled in an atmosphere of the bromine-compound without undergoing any alteration. Bromide of vinyl, freed from every trace of adhering dibromide of ethylene by repeated distillation at a low temperature, and subsequent washing with lukewarm water, was therefore enclosed, together with triethylphosphine, in a strong glass tube. No change was perceptible after two days' digestion at 100°; and it was only on the third day that a thin layer of viscid matter began to separate at the bottom of the tube. The digestion was then continued at a higher temperature; and after the mixture had been exposed for three days longer to a temperature varying from 160° to 180°, about half the fluid was found to be converted into a solid mass, while a limpid liquid floated on the top. On opening the tube, cooling it well at the time, the liquid effervesced strongly, and a gas escaped which burned with a green-edged flame, and appeared to consist, partly at all events, of the vapour of unaltered bromide of vinyl. In subsequent repetitions of the experiment, it frequently happened that the tubes were shattered by the sudden expansion of the compressed gas; hence probably permanent gases are formed in the reaction. The liquid decanted from the solid proved to be a mixture of undecomposed bromide of vinyl with free phosphorus-base; the solid mass was found to consist of several bodies. On dissolving it in water, a rather small quantity of a sparingly soluble, beautifully crystalline, nacreous salt separated out, the composition of which is at present undetermined. By treatment of the filtered solution with oxide of silver, a strongly alkaline liquid was produced, which, when neutralized with hydrochloric acid and precipitated with dichloride of platinum, gave at once the amorphous yellow platinum-salt easily soluble in dilute hydrochloric acid.

On analysis, this platinum-salt furnished the following results. Analyses I. and II. were made with the salt obtained by the action of bromide of vinyl on triethylphosphine. The platinum-determination III. refers to a salt prepared with the product of the action of heat on the hydrated diphosphonium.

I. 0·5717 grm. of platinum-salt gave 0·5211 grm. of carbonic acid and 0·2538 grm. of water.

II. 0·7623 grm. of platinum-salt, decomposed with hydrosulphuric acid, &c., gave 0·2228 grm. of platinum.

III. 0·6531 grm. of platinum-salt, analysed in the same manner, gave 0·1895 grm. of platinum.

The percentages corresponding to these analytical numbers are exactly those of the platinum-salt of the ethylene-diphosphonium.

$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2, 2PtCl_2.$$

	Theory.		Experiment.		
			I.	II.	III.
C_{14}	168	24·91	24·85	——	——
H_{34}	34	5·05	4·93	——	——
P_2	62	9·19	——	——	——
Pt_2	197·4	29·27	——	29·23	29·01
Cl_6	213	31·58	——	——	——
	674·4	100·00			

Nevertheless the two substances are not identical. In addition to the difference in the physical properties and in the behaviour with dilute hydrochloric acid, the two salts exhibit other well-defined marks of distinction. The crystalline salt is perfectly insoluble in water, even when boiling. The amorphous salt dissolves readily, and is deposited again on cooling in the same amorphous condition. In designating this peculiar molecular variety as paradiphosphonium-compound, I simply wish to distinguish it from the salt of the ordinary diphosphonium, without giving any opinion respecting the nature of the difference. The existence of the diphosphonium-compounds in the crystalline and in the amorphous condition, reminds us of the behaviour of some of the native organic bases under the influence of heat. It is well known that several of these substances, which are remarkable for their powers of crystallization, are rendered perfectly amorphous when heated for some time above their melting-point.

As might have been expected, the paradiphosphonium-compounds are slowly and gradually reconverted into the ordinary diphosphonium-salts *.

The hydrated paradiphosphonium, when separated from the platinum-compound by successive treatment with sulphuretted hydrogen and oxide of silver, yields with hydriodic acid a gummy mass which only gradually assumes the crystalline form. By a considerable number of recrystallizations, the characteristic di-iodide was ultimately obtained with all its properties; when converted, by treatment with chloride of silver, into the dichloride, and precipitated by dichloride of platinum, it immediately yielded the well-known crystalline precipitate so frequently mentioned in this paper. In order to fix by numbers this transition, and more especially the formation of diphosphonium-compounds by the action of bromide of vinyl upon triethylphosphine, the soluble bromide obtained in the reaction between the two last-named bodies was successively treated with oxide of silver and hydriodic acid. The iodide, after numerous crystallizations from alcohol, gave on analysis the following numbers:—

* In several experiments, the reaction between bromide of vinyl and triethylphosphine gave rise to the formation of a mixture of the amorphous and crystalline diphosphonium-compounds.

I. 0·3388 grm. of iodide, having a slightly yellowish tint, gave 0·4017 grm. of carbonic acid and 0·2077 grm. of water.

II. 0·2470 grm. of iodide gave 0·2255 grm. of iodide of silver.

The formula

$$C_{14}H_{34}P_2I_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' I_2$$

requires

	Theory.		Experiment.	
			I.	II.
C_{14}	168	32·43	32·34	——
H_{34}	34	6·57	6·81	——
P_2	62	11·97	——	——
I_2	254	49·03	——	49·33
	518	100·00		

This result was unequivocally confirmed by the analysis of the corresponding crystalline platinum-salt.

0·3550 grm. of the salt gave 0·3297 grm. of carbonic acid and 0·1650 grm. of water, representing 25·33 per cent. of carbon and 5·16 per cent. of hydrogen. The theoretical percentages are 24·91 of carbon and 5·05 of hydrogen.

The transition of a diphosphonium-compound from the crystalline to the amorphous, and from the amorphous to the crystalline condition, appears intelligible enough*. The transformation of the oxethylated monophosphonium, however, into a diphosphonium-compound, and the formation of the latter by the action of bromide of vinyl upon triethylphosphine, claims our attention for a moment.

The conversion of the hydrate of oxethyl-triethylphosphonium† into the hydrated diphosphonium is readily understood, if we remember that two molecules of the former contain the elements of one molecule of the latter and of one molecule of ethylene-alcohol:

$$2\left[\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\H\end{matrix}\right\}O\Big] = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]\\H_2\end{matrix}\right\}O_2 + C_2H_6O_2.$$

I am unable to say whether the group $C_2H_6O_2$ actually separates as ethylene-alcohol, or, which is more probable, in the form of water and oxide of ethylene, or even of aldehyde. Material and patience began to fail when I had reached this point, and I must reserve the decision of this question to later experiments‡.

* The diphosphonium-salt, which is formed by the action of sulphocyanate of ethylene upon triethylphosphine (see page 36), likewise, in the first place, yields the amorphous platinum-salt when precipitated by dichloride of platinum.

† I need scarcely mention that the purity of the compound used in my experiments had been established by a special analysis. When prepared from imperfectly purified bromethylated bromide, the oxethylated base is apt to contain minute quantities of the hydrate of the diphosphonium.

‡ The convertibility of the oxethylated triethylphosphonium-salts into diatomic compounds has induced

The same remark applies to the final elucidation of the reaction between triethylphosphine and bromide of vinyl, which, as I have pointed out, likewise gives rise to the formation of diphosphonium-compounds. Two molecules of triethylphosphine and two molecules of bromide of vinyl contain the elements of one molecule of dibromide of the ethylene-diphosphonium and one molecule of acetylene:

$$2[(C_2H_5)_3P] + 2C_2H_3Br = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2 + C_2H_2;$$

and experiment proves that a considerable amount of permanent gas is generated in this reaction; but there are other products formed, and it would be idle to dwell any longer on the interpretation of these unfinished observations.

In conclusion, I append Q. SELLA's crystallographical examination of the iodide of tetrethylphosphonium, to which I have alluded in the latter portion of this paper, and also the results obtained by him in measuring the corresponding platinum-salt.

Crystalline Form of Iodide of Tetrethylphosphonium.

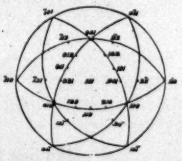
"System rhombohedric:—

$$111, 100 = 59° 32'.$$

Forms observed:—

$111, 10\bar{1}, 100, 110, 210, 31\bar{1}$ (Fig. 47).

Fig. 47.



Angles.	Calculated.	Observed.
$111, 10\bar{1}$	= 90° 0′	89° 29′
$111, 100$	= 59 32	——
$111, 110$	= 40 22	40 22
$111, 210$	= 44 28	44 28
$111, 31\bar{1}$	= 63 0	63 2
$10\bar{1}, 01\bar{1}$	= 60 0	60 7
$10\bar{1}, 100$	= 41 43	41 44
$10\bar{1}, 010$	= 90 0	90 2
$10\bar{1}, 110$	= 55 53	55 58
$10\bar{1}, 101$	= 90 0	89 59
$10\bar{1}, 210$	= 45 32	45 30

---

me to try whether the action of triethylphosphine upon them would accomplish this transformation:

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\H\end{matrix}\right\}O + (C_2H_5)_3P = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]''\\H_2\end{matrix}\right\}O_2.$$

But even when heated up to 150°, the two bodies remain unaltered; nor is there any action when the oxide is replaced by the bromide of oxethyl-triethylphosphonium.

Angles.		Calculated.	Observed.
$10\bar{1}$, 120	=	69° 30′	69° 33′
$10\bar{1}$, $31\bar{1}$	=	27 0	26 58
$10\bar{1}$, $13\bar{1}$	=	63 33	63 33
100, 010	=	96 34	96 31
100, 110	=	48 17	48 15
100, 011	=	99 54	——
100, 210	=	27 47	27 48
100, 120	=	68 47	68 42
100, 021	=	99 16	——
100, $31\bar{1}$	=	26 27	26 26
100, $13\bar{1}$	=	76 42	76 5
100, $\bar{1}31$	=	115 47	——
110, 101	=	68 14	68 3
110, 210	=	20 30	20 27
110, 201	=	57 3	——
110, 102	=	81 19	——
110, $31\bar{1}$	=	32 16	——
110, $3\bar{1}1$	=	69 46	——
110, $1\bar{1}3$	=	98 51	——
210, 120	=	41 0	40 54
210, 201	=	41 0	——
210, 021	=	74 41	——
210, 012	=	88 56	——
210, $31\bar{1}$	=	18 32	18 34
210, $13\bar{1}$	=	50 30	——
210, $\bar{1}31$	=	89 20	——
$31\bar{1}$, $13\bar{1}$	=	52 55	52 52
$31\bar{1}$, $3\bar{1}1$	=	52 55	52 59
$31\bar{1}$, $\bar{1}31$	=	101 0	101 2
$31\bar{1}$, $\bar{1}13$	=	126 0	126 4

According to NAUMANN:—

$R = 83° 26'$

Forms observed:—

$0R$; $\infty P2$; R; $-\frac{1}{3}R$; $\frac{2}{3}P2$; $\frac{1}{3}P2$.

According to Weiss:—

$$a=0{\cdot}6793$$

Forms observed:—

$$\infty a:\infty a:\infty a:c;\quad a:\tfrac{1}{3}a:a:\infty c;\quad \infty a:a:a:c;\quad \infty a':a':a':\tfrac{1}{3}c;$$
$$a:\tfrac{1}{3}a:a:\tfrac{1}{3}c;\quad a:\tfrac{1}{3}a:a:\tfrac{1}{3}c.$$

According to Levy:—

$$\mathrm{P\,P}=83^\circ\ 26'.$$

Forms observed:—

$$a',\ d,\ \mathrm{P},\ b',\ b^2,\ e_3.$$

Fig. 48.

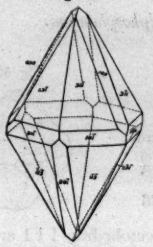


Fig. 49.

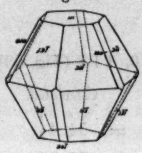
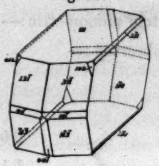


Fig. 50.



Combinations observed:—

$3\,1\,\bar{1}$; $1\,0\,0$, $1\,0\,\bar{1}$ (Fig. 48).
$3\,1\,\bar{1}$, $1\,1\,1$, $1\,0\,0$ (Fig. 49).
$3\,1\,\bar{1}$, $1\,1\,1$, $1\,0\,\bar{1}$; $1\,0\,0$ (Fig. 50).
$3\,1\,\bar{1}$, $1\,1\,0$, $1\,0\,0$; $1\,0\,\bar{1}$, $2\,1\,0$ (Figs. 51 and 52).
$3\,1\,\bar{1}$, $1\,0\,0$, $1\,1\,0$; $1\,0\,\bar{1}$, $2\,1\,0$, $1\,1\,1$.

The crystals prepared by treating triethylphosphine with iodide of ethyl exhibit the forms Figs. 51 and 52.

Fig. 51.

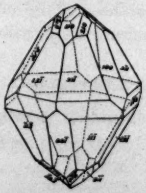
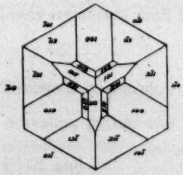


Fig. 52.



The crystals obtained by submitting the hydrated diphosphonium to the action of heat, and neutralizing the alkaline residuary product with hydriodic acid, have the form Fig. 48, when rather large and slightly yellow, and the forms Figs. 49 and 50, when minute and perfectly white.

The crystals of the form Fig. 50 are most frequent; they seem to have adhered to the vessel with one of the larger faces of the prism $1\,0\,\bar{1}$.

Crystals distinct. Lustre on the faces, except 1 1 1, very great.

Crystals optically positive. The indices of refraction are for the ordinary ray $\omega = 1{\cdot}660$, for the extraordinary ray $\epsilon = 1{\cdot}668$.

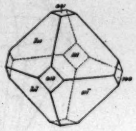
The crystals of iodide of tetrethylphosphonium are isomorphous with those of iodide of silver. In the latter substance, 1 1 1, 1 0 0 = 58° 27′, instead of 59° 32′, found in the tetrethylphosphonium-salt. Both salts have the same hexagonal habitus, and both are optically positive."

Crystalline Form of the Platinum-salt of Tetrethylphosphonium.

"System monometric:—

Forms observed:—

Fig. 53.



1 0 0, 1 1 1 (Fig. 53).

Angles.		Calculated.	Observed.
0 0 1, 1 1 1	=	54° 44′	54° 40′
1 1 1, 1 1 $\bar{1}$	=	70 32	70 36

The faces of the cube 1 0 0 are very brilliant; those of the octohedron 1 1 1 are often hollow.

No influence on polarized light.

Colour orange-red."

XXIV. *Contributions to the History of the Phosphorus-Bases.*

By AUGUSTUS WILLIAM HOFMANN, *F.R.S.*

Received June 21,—Read June 21, 1860.

THIRD MEMOIR.

PHOSPHAMMONIUM AND PHOSPHARSONIUM-, DIARSONIUM- AND ARSAMMONIUM-COMPOUNDS.

IN the former section of this inquiry, I have endeavoured to trace the history of the bodies which are generated by the mutual action of triethylphosphine and dibromide of ethylene. I have endeavoured, as far as possible, to fix with precision the several phases of this reaction, and carefully studied its principal products, the history of which appears to open the clearest perception of the nature of the polyatomic ammonias, and more especially of their connexion with the monatomic bases. The four saline compounds which, in accordance with the indications of theory, are formed by the action of dibromide of ethylene upon triethylphosphine, the bromides of the bromethylated, oxethylated, and vinylated monophosphonium, and of ethylene-diphosphonium represent, in the phosphorus-series, as well as in the nitrogen- and arsenic-series, four classes of salts, the individual terms of which admit of being constructed in unlimited number and endless variety.

The following pages are devoted to the consideration of several compounds belonging to these four principal groups. The examination of the mixed diatomic bases of the phosphorus-nitrogen, phosphorus-arsenic- and arsenic-nitrogen-series, have more especially fixed my attention. Before, however, proceeding to a detailed account of these substances, which form more particularly the subject of this paper, a few experiments may still be briefly mentioned which are even more closely connected with the observations recorded in the previous memoir.

ACTION OF DICHLORIDE OF ETHYLENE ON TRIETHYLPHOSPHINE.

It is precisely analogous to that of dibromide of ethylene, giving rise to the two compounds—

$$C_8 H_{19} P Cl_2 = [(C_2 H_4 Cl)(C_2 H_5)_3 P] Cl, \text{ and}$$

$$C_{14} H_{34} P_2 Cl_2 = \left[(C_2 H_4)'' \begin{matrix} (C_2 H_5)_3 P \\ (C_2 H_5)_3 P \end{matrix} \right]'' Cl_2.$$

If the reaction be suffered to go on to the end under the influence of heat, the resulting white crystalline mass consists almost entirely of the diphosphonium-compound; no

matter in what proportions the two bodies may be mixed, or whether they act upon one another in absence or in presence of alcohol or ether. To obtain the monatomic compound, a mixture of triethylphosphine with a very large excess of chloride of ethylene must be left to itself for some days. The white crystalline needles, which the liquid deposits, are mixed even then with a considerable quantity of the diphosphonium-compound; but on treating their solution with dichloride of platinum, and leaving the pale-yellow precipitate, which exhibits an unmistakeable diphosphonic character, at rest for some hours, it becomes traversed by a number of deep orange-yellow crystalline stars, which may easily be separated from the yellow powder by mechanical rinsing. By boiling the yellow powder with water, an additional quantity of this orange-yellow salt is obtained, which may be purified, together with the first portion, by recrystallization. This salt resembles in most respects the platinum-salt of bromethylated triethylphosphonium; it is, however, somewhat more soluble, and exhibits a more decided tendency to assume the octohedral character. As the properties of this body plainly show that it is the platinum-salt of chlorethylated triethylphosphonium,

$$C_8 H_{19} P Pt Cl_4 = [(C_2 H_4 Cl)(C_2 H_5)_3 P] Cl, Pt Cl_2,$$

I have contented myself with determining the amount of platinum contained in it.

0·3470 grm. of platinum-salt, decomposed with hydrosulphuric acid, &c., gave 0·089 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Phosphonium . . .	181·5	46·94	——
1 equiv. of Platinum	98·7	25·52	25·64
3 equivs. of Chlorine	106·5	27·54	——
1 equiv. of Platinum-salt . . .	386·7	100·00	

The chloride prepared from the needle-shaped platinum-salt by sulphuretted hydrogen yielded, when treated with oxide of silver, a caustic liquid, which, after addition of hydrochloric acid and dichloride of platinum, deposited the well-known octohedra of the oxethylated phosphonium-salt:

$$[(C_2 H_5 O)(C_2 H_5)_3 P] Cl, Pt Cl_2.$$

No doubt could exist respecting the nature of the sparingly soluble diphosphonium-platinum-salt. It was nevertheless recrystallized from boiling hydrochloric acid and identified by analysis.

I. 0·5005 grm. of platinum-salt gave 0·4617 grm. of carbonic acid and 0·2139 grm. of water.

II. 0·5240 grm. of platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0·1525 grm. of platinum.

The formula

$$C_{14} H_{34} P_2 Pt_2 Cl_6 = \left[(C_2 H_4)'' \begin{matrix} (C_2 H_5)_3 P \\ (C_2 H_5)_3 P \end{matrix} \right]'' Cl_2, 2\, Pt Cl_2$$

requires the following numbers:—

	Theory.		Experiment.	
			I.	II.
C_{14}	168	24·91	25·16	——
H_{34}	34	5·05	4·74	——
P_2	62	9·19	——	——
Pt_2	197·4	29·27	——	29·10
Cl_6	213	31·58	——	——
	674·4	100·00		

The compounds of chlorethylated triethylphosphonium are likewise formed under conditions similar to those which have already been mentioned as leading to the reproduction of the bromethylated from the oxethylated salt. On subjecting the chloride of oxethylated triethylphosphonium to the influence of pentachloride of phosphorus, a violent reaction takes place, attended with evolution of vapours of oxychloride of phosphorus. If the chloride of phosphorus be added by small portions till no further action is perceptible, and the mixture be then digested till the hydrochloric acid, the oxychloride, and any excess of pentachloride are driven off, the chloride of the chlorethylated compound remains in the retort.

$$[(C_2H_5O)(C_2H_5)_3P]Cl + PCl_5 = POCl_3 + [(C_2H_4Cl)(C_2H_5)_3P]Cl + HCl.$$

To fix the nature of this reaction by a number, the solution of the residual chloride was precipitated with dichloride of platinum. On recrystallizing the platinum-precipitate from boiling water, the beautiful needles characteristic of the chlorethylated compound immediately made their appearance.

By analysis,

0·4122 grm. of platinum-salt gave 0·1065 grm. = 25·83 per cent. of platinum.

The formula

$$[(C_2H_4Cl)(C_2H_5)_3P]Cl, PtCl_2$$

requires 25·52 per cent. of platinum.

Monochlorinated chloride of ethyl acts on triethylphosphine like dichloride of ethylene. At the common temperature, and with a large excess of the chlorinated compound, the chloride of chlorethyl-triethylphosphonium is produced, which was easily identified by the reaction with excess of nitrate of silver and ammonia, repeatedly mentioned in the previous memoir. At the temperature of 100°, and with a considerable excess of triethylphosphine, crystals of the dichloride of ethylene-diphosphonium are soon deposited. The nature of the latter was fixed by the preparation of the characteristic platinum-salt, and of the beautifully crystallized di-iodide.

Action of Di-iodide of Ethylene on Triethylphosphine.

The two bodies, in the absence of solvents, act upon one another with explosive violence. The heat evolved causes the iodide of ethylene to resolve itself into ethylene and iodine, which unites directly with the phosphorus-base. If the violence of the

action be diminished by admixture of alcohol, a white crystalline mass is obtained consisting almost entirely of the hydriodate of the phosphorus-base.

If the compounds

$$[(C_2H_4I)(C_2H_5)_3P]I \text{ and}$$

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2$$

are likewise formed, they must be present in extremely small quantities only. The crystals, dissolved in water and decomposed by baryta, left, after the triethylphosphine had been removed by ether, the iodine by oxide of silver, and the baryta by means of carbonic acid, scarcely traces of an organic compound. The triethylphosphine evidently acts upon iodide of ethylene just like an alcoholic solution of potassa, the chief phase of the reaction doubtless consisting in the transformation,

$$(C_2H_5)_3P + (C_2H_4)''I_2 = [(C_2H_5)_3HP]I + C_2H_3I.$$

I should not omit to mention, however, that the production of iodide of vinyl (C_2H_3I) was not demonstrated by a special experiment. There was some probability of an iodethylated triethylphosphonium-compound being formed by the action of iodide of phosphorus on the chloride or iodide of the oxethylated metal; but these bodies do not act on one another.

Hybrids of Ethylene-Diphosphonium.

In a former paragraph, I mentioned as a fact of peculiar interest, the formation of the dibromide of hexethylated ethylene-diphosphonium by the reaction

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3P = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

The study of this reaction naturally led me to try that of trimethylphosphine on the bromide of bromethylated triethylphosphonium, which I had a right to expect would thus be converted into the dibromide of ethylene-trimethyl-triethyldiphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3P = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

Action of Trimethylphosphine on Bromide of Bromethyl-triethylphosphonium.

These two bodies act upon each other with the greatest energy, and moreover exactly in the manner indicated by theory. The resulting compound was, of course, examined only as far as necessary to establish the character of the reaction. The bromide of the hybrid diphosphonium is more soluble than the similar diphosphonium-compound previously described, which in other respects it greatly resembles. Oxide of silver eliminates the extremely caustic base,

$$C_{11}H_{30}P_2O_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)_3(C_2H_5)_3P_2]''\\H_2\end{matrix}\right\}O_2,$$

which yields with hydrochloric acid and dichloride of platinum, a pale-yellow platinum-salt,

$$C_{11}H_{28}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2,$$

crystallizing in scales from boiling water. I have contented myself with determining the amount of platinum in this salt.

0·4794 grm. of platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0·1502 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Diphosphonium	222·0	35·10	——
2 equivs. of Platinum . .	197·4	31·22	31·33
6 equivs. of Chlorine . .	213·0	33·68	——
1 equiv. of Platinum-salt .	632·4	100·00	

The salts of the hybrid diphosphonium crystallize like those of the corresponding hexethylated compound, but, as far as they have been examined, are somewhat more soluble; this remark applies especially to the di-iodide.

It seemed worth while to try whether the bromide of bromethylated triethylphosphonium was capable of fixing a molecule of *phosphoretted hydrogen*. I found, however, that the two bodies do not act upon one another. Phosphoretted hydrogen gas, passed through the alcoholic solution of the bromide, either cold or boiling, did not seem to affect it in any way.

Action of Dibromide of Ethylene on Trimethylphosphine.

This reaction exhibits a repetition of all the phenomena observed in that which takes place between the dibromide and triethylphosphine. The process is completed, if possible, even sooner than in the ethyl-series. The lower boiling-point and overpowering odour of the trimethylphosphine, render it advisable to mix the materials with considerable quantities of alcohol or ether; moreover, on account of the extreme oxidability of the phosphorus-compound, it is necessary to operate in vessels filled with carbonic acid and immediately sealed before the blowpipe. After digestion for a short time at 100°, the mixture of the two liquids solidifies to a hard, dazzling white, crystalline mass, containing the two bromides,

$$C_5 H_{13} P Br_2 = [(C_2 H_4 Br)(C H_3)_3 P] Br, \text{ and}$$

$$C_8 H_{22} P_2 Br_2 = \left[(C_2 H_4)'' \begin{matrix}(C H_3)_3 P \\ (C H_3)_3 P\end{matrix}\right]'' Br_2,$$

one or the other predominating, according to the proportions in which the two bodies were allowed to act upon one another.

It is not difficult to establish by numbers the formation of these two bodies.

Bromide of Bromethyl-trimethylphosphonium.—When a solution of trimethylphosphine in absolute alcohol, mixed with a very large excess of dibromide of ethylene, is exposed for some hours to a temperature of from 50° to 60°, the liquid on cooling deposits well-formed crystals. It is desirable not to pass this temperature; at the boiling-point of water the mixture turns brown, in consequence of secondary reactions. One or two crystallizations from absolute alcohol render the crystals perfectly pure; they exhibit in this state the chemical and physical characters of the corresponding ethylated body,

possessing, however, a different crystalline form. I have fixed the composition of this substance by the determination of the bromine accessible to silver-salts.

0·3980 grm. of bromide, precipitated by nitrate of silver, gave 0·2820 grm. of bromide of silver.

The formula

$$C_5 H_{13} P Br_2 = [(C_2 H_4 Br)(C H_3)_3 P] Br,$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium	184	69·70	——
1 equiv. of Bromine . .	80	30·30	30·16
1 equiv. of Bromide . .	264	100·00	

This result was confirmed by several analyses of the corresponding

Platinum-salt.—This is easily formed by treating the bromide with chloride of silver, when a crystallizable chloride is produced, which yields with dichloride of platinum splendid orange-yellow needles, containing

$$C_5 H_{13} P Br Pt Cl_3 = [(C_2 H_4 Br)(C H_3)_3 P], Pt Cl_2.$$

I. 0·5440 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1390 grm. of platinum.

II. 0·495 grm. of platinum-salt, analysed in the same manner, gave 0·126 grm. of platinum.

III. 0·304 grm. of platinum-salt gave 0·077 grm. of platinum.

	Theory.		Experiment.		
			I.	II.	III.
1 equiv. of Phosphonium . .	184·0	47·27	——	——	——
1 equiv. of Platinum . . .	98·7	25·36	25·55	25·45	25 33
3 equivs. of Chlorine . . .	106·5	27·37	——	——	——
1 equiv. of Platinum-salt . .	389·2	100·00			

I have already mentioned that the bromide of bromethyl-trimethylphosphonium crystallizes differently from the bromide of the ethylated body. Whilst the latter is obtained in rhombic dodecahedrons, the methylated bromide affects forms belonging to the trimetric system. Quintino Sella has made the following examination of this compound:—

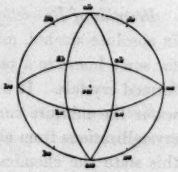
"System trimetric:—

$$100, 110 = 60° 24';$$
$$001, 101 = 22° 9'.$$

Forms observed:—

100, 010, 001, 110, 211 (Fig. 54).

Fig. 54.



Angles.		Calculated.	Observed.
100, 010	=	90° 0′	90° 2′
100, 001	=	90 0	89 58
100, 110	=	60 24	60 26
100, 211	=	56 30	56 27
010, 001	=	90 0	90 6
010, 110	=	29 36	29 36
010, 211	=	60 56	60 55
001, 110	=	90 0	89 55
001, 211	=	47 19	47 17
110, $\bar{1}10$	=	59 12	59 12
110, 211	=	45 59	45 45
110, $\bar{2}11$	=	81 23	81 21
211, $\bar{2}11$	=	67 0	67 6
211, $2\bar{1}1$	=	58 7	58 10
211, $\bar{2}\bar{1}1$	=	94 39	94 34

According to Naumann:—

$$a:b:c = 0{\cdot}4071 : 1 : 0{\cdot}5681.$$

Forms observed:—

$$\infty\breve{P}\infty,\ \infty\bar{P}\infty,\ 0P,\ \infty P,\ 2\breve{P}2.$$

According to Weiss:—

$$a:b:c = 1 : 0{\cdot}5681 : 0{\cdot}4071.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:b:\infty c;\quad \infty a:\infty b:c;\quad a:b:\infty c;\quad \tfrac{1}{2}a:b:c.$$

According to Levy:—

$$M\,M = 120° 48';\quad b:h = 1 : 0{\cdot}3539.$$

Forms observed:—

$$g', h', P, M, e_3.$$

Combinations observed:—

100, 010, 001; 110 (Fig. 55).
100, 010, 001; 110, 211 (Fig. 56).
110, 001; 100 (Fig. 57).
110, 001; 100, 010, 211 (Fig. 58).
001, 010, 211 (Fig. 59).

Fig. 55.

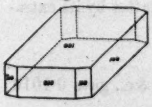


Fig. 56.

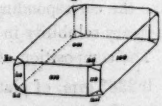


Fig. 57.

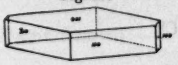


Fig. 58.

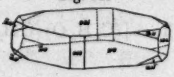
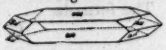


Fig. 59.



The crystals are generally tabular, as in the above figures; sometimes, however, they are elongated in the direction [0 0 1], and then the faces are most unequally developed. Figs. 60 and 61, and, again, Figs. 62 and 63 exhibit two very remarkable crystals of this kind.

The faces of the form 2 1 1 are generally very unequally developed, and some are actually wanting. In the crystals Figs. 60 and 61, and, again, Figs. 62 and 63, only two out of the eight faces 2 1 1 were well developed. The six others were wanting, or could but just be traced.

Fig. 60.

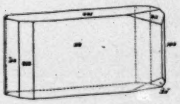


Fig. 61.

Fig. 62.

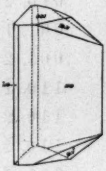
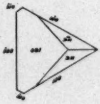


Fig. 63.



The lustre of the faces 0 0 1 is glassy, or even pearly. The lustre of the other faces is less marked, and more fatty.

Cleavages 0 0 1 easily obtained and rather perfect; 1 1 0 easily obtained, but fibrous.

The axes of optical elasticity, in the order of magnitude, are [0 0 1], [1 0 0], [0 1 0]."

Compounds of Oxethyl-trimethylphosphonium.

The liquid filtered from the sulphide of platinum in the three analyses of the platinum-salt of bromethyl-trimethylphosphonium above given, yielded by evaporation the extremely soluble and deliquescent chloride. This salt has not been analysed; but I have transformed it, by oxide of silver, into the corresponding oxethylated compound,

$$C_5H_{15}PO_2 = \left.\begin{matrix}[(C_2H_5O)(CH_3)_3P]\\ H\end{matrix}\right\}O.$$

The caustic liquid is converted by hydrochloric acid into the easily soluble chloride corresponding to the hydrate; this chloride, treated with dichloride of platinum, yields the platinum-salt of oxethylated trimethylphosphonium, which crystallizes in octohedra, like the corresponding ethyl-compound, but is distinguished from the latter by its extraordinary solubility in water.

The composition of this salt was fixed by a platinum-determination.

0·3383 grm. of platinum-salt, precipitated with hydrosulphuric acid, &c., gave 0·1010 grm. of platinum.

The formula

$$C_5H_{14}POPtCl_3 = [(C_2H_5O)(CH_3)_3P]Cl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium . . .	121	37·09	——
1 equiv. of Platinum	98·7	30·26	29·86
3 equivs. of Chlorine	106·5	32·65	——
1 equiv. of Platinum-salt . . .	326·2	100·00	

SALTS OF ETHYLENE-HEXMETHYL-DIPHOSPHONIUM.

Dibromide.—This salt is formed when dibromide of ethylene is treated with an excess of trimethylphosphine. The reaction is rapidly accomplished at the temperature of boiling water. The salt resembles the dibromide of the ethyl-series in its properties. It is extremely soluble, and was only once obtained in well-defined crystals, which were analysed and determined. Many efforts were made to produce these well-formed crystals a second time, but without success.

0·2940 grm. of dibromide gave 0·3246 grm. of bromide of silver, corresponding to the formula

$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Br_2,$$

as seen by the following comparison of the theoretical and experimental percentages of bromine:—

	Theory.		Experiment.
1 equiv. of Diphosphonium . . .	180	52·94	——
2 equivs. of Bromine	160	47·06	47·00
1 equiv. of Dibromide	340	100·00	

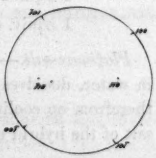
The following are the details of SELLA's crystallographical determination:—

"System monoclinic:—

$100, 101 = 17° 45'$; $101, 001 = 20° 4'$; $010, 111 = 57° 47'$.

Forms observed:— Fig. 64.

$001, 110, \bar{1}01$ (Fig. 64).



Angles.		Calculated.	Observed.
$110, 001$	=	58° 22′	58° 22′
$001, \bar{1}01$	=	80 52	80 50
$110, \bar{1}10$	=	83 13	83 12
$110, \bar{1}01$	=	108 38	108 38

According to NAUMANN:—

$a:b:c = 1·1255:1:0·5445$; $\gamma = 37° 49'$.

Forms observed:—

$0P$, ∞P, $P\infty$.

According to Weiss:—

$$a : b : c = 1 : 0{\cdot}5445 : 1{\cdot}1255; \quad a\,o\,c = 142^\circ\ 11'.$$

Fig. 65.

Forms observed:—

$$\infty a : \infty b : c; \quad a : b : \infty c; \quad -a : \infty b : c.$$

According to Levy;—

$$M\,M = 83^\circ\ 13'; \quad M\,P = 121^\circ\ 38'; \quad b : h = 1 : 0{\cdot}9884.$$

Forms observed:—

P, M, a'.

Combinations observed:—

0 0 1, 1 1 0 (Fig. 65).

The face $\bar{1}\,0\,1$ has not been directly observed, but was found to be a cleavage. There is also another cleavage 0 0 1, as distinct and easily obtained as $\bar{1}\,0\,1$."

The dibromide of hexmethylated ethylene-diphosphonium, treated with oxide of silver, yields the corresponding hydrate,

$$C_8H_{24}P_2O_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)_6P_2]'' \\ H_2\end{matrix}\right\}O_2,$$

which forms with acids a series of salts resembling the corresponding ethyl-compounds. Of these I have briefly examined the di-iodide and the platinum-salt.

Di-iodide.—The base neutralized with hydriodic acid furnishes a salt crystallized in difficultly soluble needles, surpassing in beauty the corresponding body in the ethyl-series.

0·3515 grm. of salt gave 0·3775 grm. of iodide of silver, leading to the formula

$$C_8H_{22}P_2I_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P \\ (CH_3)_3P\end{matrix}\right]''I_2,$$

which requires

	Theory.		Experiment.
1 equiv. of Diphosphonium . . .	180	41·43	——
2 equivs. of Iodine	254	58·57	57·92
1 equiv. of Di-iodide	434	100·00	

Platinum-salt.—This is an apparently amorphous precipitate, which is nearly insoluble in water, dissolves with extreme slowness in boiling hydrochloric acid, and separates therefrom on cooling in golden-yellow laminæ, very much like those of the platinum-salt of the hybrid ethylene-trimethyl-triethyl-diphosphonium. It consists of

$$C_8H_{22}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P \\ (CH_3)_3P\end{matrix}\right]''Cl_2, 2PtCl_2.$$

I. 0·4940 grm. of platinum-salt gave, when precipitated by sulphuretted hydrogen, &c., 0·1650 grm. of platinum.

II. 0·5730 grm. of platinum-salt gave 0·1900 grm. of platinum.

	Theory.		Experiment.	
			I.	II.
1 equiv. of Diphosphonium .	180·0	30·49	——	——
2 equivs. of Platinum . . .	197·4	33·43	33·40	33·16
6 equivs. of Chlorine . . .	213·0	36·08	——	——
1 equiv. of Platinum-salt . .	590·4	100·00		

SERIES OF MIXED DIATOMIC BASES.

The investigation of the intimate relation which unites the bromethylated monophosphonium with the ethylene-diphosphonium-compounds, together with the establishment of the easy transition from the monatomic to the diatomic series, naturally suggested the idea of subjecting the bromethylated bromide, which forms the starting-point of the whole investigation, to the action of *monamines*, *monarsines*, and *monostibines*, in the expectation that diatomic bases would be formed containing nitrogen, arsenic, and antimony, side by side with phosphorus, and equivalent to it in chemical value and character. How far this expectation has been realized may be seen from the following experiments.

PHOSPHAMMONIUM-COMPOUNDS.

Action of Ammonia on Bromide of Bromethyl-triethylphosphonium.

In alcoholic solution, these two bodies act upon one another at ordinary temperatures, the reaction being indicated by considerable evolution of heat. To ensure complete transformation, the mixture is digested at 100° for half an hour in sealed tubes. On evaporating the alcohol and the excess of ammonia, there remains an extremely deliquescent saline mass, which crystallizes with difficulty. To remove small quantities of ammonia which may be present in the form of bromide of ammonium, the solution of the saline residue is treated with excess of oxide of silver, whereby a strongly alkaline liquid is set free, which may be digested on the water-bath without decomposition, so that traces of ammonia are easily driven off. Further investigation showed the presence in the caustic alkaline liquid of a base containing both phosphorus and nitrogen, viz. the hydrate of ethylene-triethylphosphammonium,

$$C_8H_{24}PNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3PH_3PN]'' \\ H_2\end{matrix}\right\}O_2.$$

The reaction between the bromethylated monophosphonium and ammonia had therefore taken place exactly as might have been expected from the behaviour of the former compound with the monophosphines:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + H_3N = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ H_3N\end{matrix}\right]''Br_2.$$

I have fixed the composition of the nitrophosphoretted base by the analysis of the platinum-salt and of the gold-salt.

Platinum-salt.—On saturating the alkaline hydrate with hydrochloric acid and adding

dichloride of platinum, a very voluminous, pale-yellow, slightly crystalline precipitate is obtained, which is difficultly soluble in boiling water, and also in boiling concentrated hydrochloric acid. The acid solution deposits well-formed prismatic crystals. The crystallization from concentrated hydrochloric acid is necessary to ensure the purity of the product; it appears that the direct precipitate contains an admixture which remains dissolved in the acid. Specimens of different preparation gave on analysis the following results:—

I. 0·6817 grm. of platinum-salt gave 0·4220 grm. of carbonic acid and 0·2256 grm. of water.

II. 0·8285 grm. of platinum-salt gave 0·5195 grm. of carbonic acid and 0·2890 grm. of water.

III. 0·3658 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1257 grm. of platinum.

IV. 0·5005 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1716 grm. of platinum.

V. 0·8835 grm. of platinum-salt, treated in the same manner, gave 0·3069 grm. of platinum.

The formula

$$C_8H_{22}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\quad N\end{matrix}\right]''Cl_2, 2PtCl_2$$

requires

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
C_8	96	16·74	16·88	17·10	——	——	——
H_{22}	22	3·84	3·67	3·87	——	——	——
P	31	5·41	——	——	——	——	——
N	14	2·44	——	——	——	——	——
Pt_2	197·4	34·43	——	——	34·28	34·36	34·73
Cl_6	213	37·14	——	——	——	——	——
	573·4	100·00					

Some of the crystals, obtained on slowly cooling a boiling solution in concentrated hydrochloric acid, were sufficiently well-formed to enable Q. Sella to examine them crystallographically. He has communicated to me the following description:—

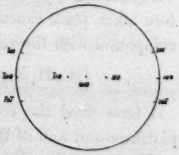
"System trimetric:—

$100, 110 = 59° 50'$; $001, 101 = 70° 38'$.

Forms observed:—

$100, 110, 101, 010$ (Fig. 66).

Fig. 66.



Angles.	Calculated.	Observed.
$100, 010$	$= 90° 0'$	$89° 40'$
$100, 110$	$= 59\ 50$	$59\ 55$

Angles.		Calculated.	Observed.
100, 101	=	19° 22′	19° 27′
010, 110	=	30 10	——
010, 101	=	90 0	——
110, $\bar{1}$10	=	60 20	60 10
110, 101	=	61 42	61 37
101, $\bar{1}$01	=	38 44	38 54

According to Naumann:—

$$a : b : c = 2{\cdot}8449 : 1 : 0{\cdot}5812.$$

Forms observed:—

$$\infty \breve{P} \infty,\ \infty \bar{P} \infty,\ \infty P,\ \breve{P} \infty.$$

According to Weiss:—

$$a : b : c = 1 : 0{\cdot}5812 : 2{\cdot}8449.$$

Forms observed:—

$$a : \infty b : \infty c;\quad \infty a : b : \infty c;\quad a : b : \infty c;\quad a : \infty b : c.$$

According to Levy:—

$$M\,M = 119° 40';\quad b : h = 1 : 2{\cdot}4596.$$

Forms observed:—

$$g', h', M, e'.$$

Combinations observed:—

100, 110, 101 (Fig. 67).

100, 110, 101; 010 (Fig. 68).

Fig. 67.

Fig. 68.

Cleavage 010 imperfect.

The faces 101 are dull, the others brilliant. The crystals are optically negative. The medium line is perpendicular to 100, and the plane of the optical axes is parallel to 001. The external angle of the optical axes appears to be about 60°.

Hardness greater than that of gypsum."

Gold-salt.—The solution of the dichloride, which is obtained by treating the crystallized platinum-salt with hydrosulphuric acid, yields with trichloride of gold a golden-yellow precipitate consisting of fine needles, which are difficultly soluble in water.

0·3845 grm. of gold-salt, precipitated by hydrosulphuric acid, &c., gave 0·1800 grm. of gold.

The formula

$$C_8H_{22}PNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\ \ N\end{matrix}\right]''Cl_2,\ 2\,AuCl_3$$

requires

	Theory.		Experiment.
1 equiv. of Phosphammonium . . .	163	19·38	——
2 equivs. of Gold	394	46·85	46·81
8 equivs. of Chlorine	284	33·77	——
1 equiv. of Gold-salt	841	100·00	

The analysis of the platinum-salt and of the gold-salt sufficiently fixes the composition of the series of diatomic phosphammonium-compounds. I have prepared some of the simple salts of this nitrophosphoretted metal, especially the dichloride, the dibromide, and the di-iodide. They all crystallize pretty well, although they are in general more soluble and less stable than the diphosphonium-salts. The diperchlorate is rather difficultly soluble, and crystallizes with facility. These salts have not been analysed. The free base likewise resembles the hydrate of the diphosphonium. Its solution is powerfully alkaline, and precipitates from most metallic salts the hydrates of the metals. The solution of the base may be concentrated on the water-bath without losing ammonia; addition of potassa to the residuary liquid separates the hydrate in oily drops, which redissolve when mixed with water.

The peculiar construction of this body induced me to examine its deportment under the influence of heat. The substitution being limited to 5 equivs. of hydrogen, the question arose whether the hydrate could be distilled in the form of a phosphamine of the formula

$$\left.\begin{matrix}(C_2H_4)''\\(C_2H_5)_2\\(C_2H_5)H\end{matrix}\right\}PN.$$

Experiment showed, however, that the base cannot be volatilized without entire decomposition; the product of distillation no longer contains a trace of the original body. Ammonia is abundantly evolved during the distillation, and at a certain stage of the process the residue contains the hydrate of vinylated triethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3PN]''\\H_2\end{matrix}\right\}O_2 = H_3N + H_2O + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\H\end{matrix}\right\}O.$$

I infer this from the analysis of an iodide obtained by neutralizing with hydriodic acid the mixed base which had been heated for some time. This salt was exceedingly soluble in water, and even in absolute alcohol, and was precipitated from the latter by addition of ether.

0·4865 grm. of iodide gave 0·416 grm. of iodide of silver.

The formula

$$C_8H_{18}PI = [(C_2H_3)(C_2H_5)_3P]I$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium . .	145	53·31	——
1 equiv. of Iodine	127	46·69	46·4
1 equiv. of Iodide	272	100·00	

The mother-liquor of this salt was freed from excess of silver and precipitated by trichloride of gold. The yellow needles were analysed.

0·6580 grm. of gold-salt gave 0·2615 grm. = 39·68 per cent. of gold.

The formula

$$C_8 H_{18} P Au Cl_4 = [(C_2H_3)(C_2H_5)_3 P] Cl, Au Cl_3$$

requires 39·24 per cent. of gold.

The deportment of the bromethylated bromide under the influence of ammonia, opens an almost unlimited series of diatomic nitrophosphoretted metals. It is only necessary to replace in the above reaction the ammonia by a monamine, in order to obtain a new metal of almost any composition which could be desired. I have produced a few bodies of this description, in order to establish experimentally the relations, which theory, resting on the observations in the ammonia-reaction, sufficiently suggests.

Action of Methylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-methyl-triethylphosphammonium.

Repetition of all the phenomena observed in the experiment with ammonia. Both substances unite on digestion,

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)H_2N = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (CH_3)H_2 & N\end{matrix}\right]''Br_2,$$

and the compound yields, on treatment with oxide of silver, the caustic base

$$C_9H_{26}PNO_2 = \left[(C_2H_4)''(CH_3)(C_2H_5)_3H_2PN\right]''\Big\}O_2.$$

I have been satisfied to fix the composition of this body by the analysis of a rather difficultly soluble platinum-compound, crystallizing from boiling water in splendid needles, frequently an inch in length. I did not succeed, however, in obtaining, either from boiling water or from boiling hydrochloric acid, crystals which could have been determined. For analysis the salt was recrystallized from boiling water.

0·3734 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1250 grm. of platinum.

The formula

$$C_9H_{24}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (CH_3)H_2 & N\end{matrix}\right]''Cl_2, 2PtCl_2$$

requires

	Theory.		Experiment.
1 equiv. of Phosphammonium . . .	177	30·13	——
2 equivs. of Platinum	197·4	33·60	33·48
6 equivs. of Chlorine	213	36·27	——
1 equiv. of Platinum-salt	587·4	100·00	

Action of Ethylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-tetrethylphosphammonium.

The two bodies unite with evolution of heat. Since the salts of the new phosphammonium crystallize very beautifully, I have not been able to resist the temptation of examining several of them somewhat more minutely.

Platinum-salt.—The crude product of the reaction, purified with oxide of silver and saturated with hydrochloric acid, furnishes, on addition of dichloride of platinum, an orange-yellow platinum-compound, crystallizing in needles very similar to those of the methyl-compound above-described. The salt, recrystallized from boiling water, gave on analysis the following numbers:—

I. 0·7544 grm. of platinum-salt gave 0·5565 grm. of carbonic acid and 0·3023 grm. of water.

II. 0·6056 grm. of platinum-salt, when treated with sulphuretted hydrogen, &c., gave 0·1964 grm. of platinum.

The formula

$$C_{10}H_{26}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5)H_2 & N\end{matrix}\right]'' Cl_2, 2\,PtCl_2$$

requires

	Theory.		Experiment.	
			I.	II.
C_{10}	120	19·96	20·12	——
H_{26}	26	4·32	4·45	——
P	31	5·15	——	——
N	14	2·33	——	——
Pt_2	197·4	32·82	——	32·43
Cl_6	213	35·42	——	——
	601·4	100·00		

Q. SELLA has determined the crystalline form of this beautiful salt.

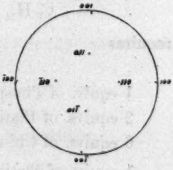
"System monoclinic:—

$100, 101 = 43° 35'$; $101, 001 = 43° 17'$; $111, 010 = 55° 36'$.

Forms observed:—

$100, 001, 110, 011$ (Fig. 69).

Fig. 69.



Angles.	Calculated.	Observed.
$100, 001$	= 86° 52′	86° 52′
$100, 110$	= 44 55	45 8
$100, 011$	= 87 47	87 38
$001, 110$	= 87 47	87 53
$001, 011$	= 44 46	44 47
$110, \bar{1}10$	= 90 10	90 10
$110, 011$	= 58 21	58 5
$110, 01\bar{1}$	= 61 59	62 11
$011, 01\bar{1}$	= 90 29	90 29

According to Naumann:—

$$a:b:c = 0{\cdot}9945 : 1 : 1{\cdot}0013; \quad \gamma = 86° 52'.$$

Forms observed:—

$$\infty P\infty, \quad 0P, \quad \infty P, \quad P\infty.$$

According to Weiss:—

$$a:b:c = 1 : 1{\cdot}0013 : 0{\cdot}9945; \quad a\,o\,c = 93° 8'.$$

Forms observed:—

$$a:\infty b:\infty c; \quad \infty a:\infty b:c; \quad a:b:\infty c; \quad \infty a:b:c.$$

According to Levy:—

$$MM = 90° 10'; \quad MP = 92° 13; \quad b:h = 1 : 0{\cdot}7027.$$

Forms observed:—

$$h', \quad P, \quad M, \quad e'.$$

Combinations observed:—

1 1 0, 0 1 1 (Fig. 70).

1 1 0, 0 1 1, 0 0 1 (Fig. 71).

1 1 0, 0 1 1, 0 0 1, 1 0 0 (Figs. 72, 73).

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Fig. 70.

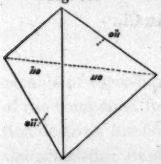


Fig. 71.

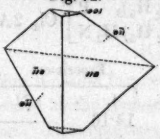


Fig. 72.

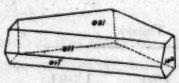
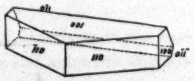


Fig. 73.



The crystals are hemihedral: the faces 0 0 1 and 1 0 0 have their parallels, but of the four faces of the forms 1 1 0 and 0 1 1 only two were observed with their corresponding parallels.

All the crystals examined exhibit the faces 1 1 0, $\bar{1}$ 1 0, and the faces 0 $\bar{1}$ 1, 0 $\bar{1}$ $\bar{1}$ (Figs. 70, 71, and 73). In a single crystal (Fig. 72) the faces $\bar{1}$ $\bar{1}$ 0, 1 $\bar{1}$ 0, and the faces 0 1 1, 0 1 $\bar{1}$ were observed. It is evident that the crystals Figs. 72 and 73 are symmetrical but not superposable.

The crystals frequently exhibit the habitus of triangular tables (Figs. 72 and 73); sometimes they are tetrahedrons (Fig. 70), or beveled tetrahedrons (Fig. 71).

The faces are very brilliant but very often rounded, so that they are apt to yield many images and a great difference in the angles.

The observed angles given in the above table are the mean of the results obtained in the measurement of six crystals.

Another difficulty in the determination of these crystals is the minute difference of the angles of the zones [0 0 1] and [1 0 0]. The results of observation are 1 1 0, $\bar{1}$ 1 0 = 90° 10′; 0 1 1, 0 1 $\bar{1}$ = 90° 29′; but I cannot affirm that the second angle is greater than the first. For distinguishing the two zones I had at my disposal only one criterion, which is of

comparatively little value. The faces designated as 1 1 0, $\bar{1}$ 1·0 are in general equally developed, but of the two others, 0 $\bar{1}$ 1 is much larger than 0 $\bar{1}$ $\bar{1}$, as seen in Fig. 73. I took it for granted that the two equally developed faces belonged to the zone [0 0 1], and the unequally developed faces to the zone [1 0 0].

The plane of polarization is not altered if the light passes through the faces 0 0 1, 0 0 $\bar{1}$ and the faces 1 0 0, $\bar{1}$ 0 0 in the direction [0 1 0].

Colour orange-red.

The minuteness of the crystals, and the difficulty of fixing them on account of their hemihedral form, has prevented me from finding their cleavages."

Gold-salt.—Golden-yellow, difficultly soluble needles, which may be recrystallized from boiling water without decomposition.

I. 0·6325 grm. of gold-salt gave 0·3285 grm. of carbonic acid and 0·1788 grm. of water.

II. 0·6963 grm. of gold-salt left after ignition 0·3160 grm. of gold. The residue of gold retained with great pertinacity a small quantity of carbon, from which it could be separated only by solution in *aqua regia*, filtration, and re-evaporation.

The analyses lead to the formula

$$C_{10}H_{26}PNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\ P\\(C_2H_5)H_2\ N\end{matrix}\right]''Cl_2, 2AuCl_3.$$

	Theory.		Experiment.	
			I.	II.
C_{10}	120	13·81	14·16	——
H_{26}	26	2·99	3·14	——
P	31	3·57	——	——
N	14	1·61	——	——
Au_2	394	45·34	——	45·38
Cl_8	284	32·68	——	——
	869	100·00		

Di-iodide.—It was prepared from the recrystallized platinum-salt by treatment with sulphuretted hydrogen, decomposition of the resulting dichloride by oxide of silver, and neutralization of the liberated base with hydriodic acid. White acicular crystals, extremely soluble in water, but not deliquescent, likewise very soluble in spirit of wine, difficultly soluble in absolute alcohol, insoluble in ether. From the alcoholic liquid, the salt is precipitated by ether in the crystalline state. From the aqueous solution, the iodide separates, on addition of potassa, in the form of oily globules, which gradually solidify with crystalline structure.

Since the examination of the phosphammonium-compounds could not have been legitimately concluded without a nitrogen-determination, the nitrogen was taken in this iodide.

I. 0·6663 grm. of di-iodide, dried *in vacuo* over sulphuric acid, gave 0·3335 grm. of ammonio-chloride of platinum.

II. 0·4680 grm. of di-iodide gave 0·4891 grm. of iodide of silver.

The formula is accordingly

$$C_{10}H_{26}PNI_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P \\ (C_2H_5)H_2 & N\end{matrix}\right]'' I_2.$$

	Theory.		Experiment.	
			I.	II.
C_{10}	120	26·97	——	——
H_{26}	26	5·84	——	——
P	31	6·97	——	——
N	14	3·14	3·14	——
I_2	254	57·08	——	56·48
	445	100·00		

The caustic base, which corresponds to the iodide, is readily obtained by oxide of silver. It presents considerable stability, and may be evaporated on the water-bath until it separates in heavy oily globules. Here again the action of heat might have given rise to the formation of a volatile phosphamine,

$$\left.\begin{matrix}(C_2H_4)'' \\ (C_2H_5)_2 \\ (C_2H_5)_2\end{matrix}\right\} PN,$$

capable of reproducing the salts from which it was derived. But, exactly as in the case of the compound formed by the coalescence of triethylphosphine and ammonia, distillation destroys the base. The deportment of this substance under the influence of heat is characteristic; its study cannot fail to assist in the general elucidation of the constitution of this class of bodies. I may, in a subsequent inquiry, find an opportunity of returning to this question.

Both methylamine and ethylamine being primary monamines, I have, in conclusion, submitted the bromethylated bromide to the action of a secondary base, viz. diethylamine, and lastly, of some tertiary bases, viz. trimethylamine and triethylamine.

Action of Diethylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-pentethylphosphammonium.

The reaction is similar to that of ethylamine; the resulting product, conveniently treated, yields a splendid platinum-salt crystallizing in rectangular plates.

Two platinum-determinations furnished the following results:—

I. 0·4900 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1557 grm. of platinum.

II. 0·6280 grm. of platinum-salt, analysed in the same manner, gave 0·1990 grm. of platinum.

These numbers correspond to the formula

$$C_{12}H_{30}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\ P\\(C_2H_5)_2\ H\ N\end{matrix}\right]''Cl_2,\ 2PtCl_2.$$

	Theory.		Experiment.	
			I.	II.
1 equiv. of Phosphammonium	219·0	34·79	——	——
2 equivs. of Platinum . . .	197·4	31·37	31·77	31·68
6 equivs. of Chlorine	213·0	33·84	——	——
1 equiv. of Platinum-salt . .	629·4	100·00		

ACTION OF TRIMETHYLAMINE ON THE BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

ETHYLENE-TRIMETHYL-TRIETHYLPHOSPHAMMONIUM-COMPOUNDS.

As to the preparation and properties, I may refer to the preceding paragraphs. It is only necessary to quote the analysis of the platinum-salt, which crystallizes in beautiful needles.

I. 0·4758 grm. of platinum-salt gave 0·3715 grm. of carbonic acid and 0·1907 grm. of water.

II. 0·7485 grm. of platinum-salt, when fused with carbonate of sodium, &c., gave 0·2415 grm. of platinum and 1·0580 grm. of chloride of silver.

The formula

$$C_{11}H_{28}PNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\ P\\(CH_3)_3\ N\end{matrix}\right]''Cl_2,\ 2PtCl_2$$

requires

	Theory.		Experiment.	
			I.	II.
C_{11}	132	21·45	21·29	——
H_{28}	28	4·55	4·45	——
P	31	5·04	——	——
N	14	2·27	——	——
Pt_2	197·4	32·08	——	32·26
Cl_6	213	34·61	——	34·96
	615·4	100·00		

The examination of this compound has induced me to perform an experiment which may here be briefly mentioned. The action of trimethylamine on dibromide of ethylene gives rise to the formation of a beautifully crystallized salt, the bromide of bromethyl-trimethylammonium, of which I have already given a fugitive sketch in the 'Proceedings of the Royal Society'*. I was curious to ascertain whether the dibromide, generated by the union of *trimethylamine* with the bromide of bromethyl-*triethyl-phosphonium*, could likewise be formed by submitting the bromide of bromethyl-*trimethyl-*

* Proceedings of the Royal Society, vol. ix. p. 293.

ammonium to the action of *triethylphosphine*:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3N = [(C_2H_4Br)(CH_3)_3N]Br + (C_2H_5)_3P$$

$$= \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)_3N\end{matrix}\right]''Br_2.$$

The bromide of bromethylated trimethylammonium is indeed readily attacked by triethylphosphine, but the change is very different from what I had expected. I intend in another paper to return to the products of this reaction.

Before leaving the history of the phosphammonium-compounds, I have briefly to allude to a peculiar deportment of the bromethylated bromide. When treating this compound with triethylamine instead of trimethylamine, expecting, of course, to observe a repetition of the phenomena so frequently witnessed, I was surprised to find that these substances, although acting with considerable energy, fail to produce the anticipated phosphammonium-compound. This unforeseen result induced me to examine this reaction repeatedly and with particular care. The result remained the same. On evaporating the alcoholic product of the reaction, and treating the concentrated solution with oxide of silver, a powerfully alkaline liquid remained, even after the expulsion of the triethylamine, considerable quantities of which were liberated. This residuary alkaline liquid, saturated with hydrochloric acid, yielded, on addition of dichloride of platinum, the beautiful octohedra of the oxethylated triethylphosphonium-platinum-salt, which was identified by analysis. The specimen which was employed in analysis IV., mentioned in the description of the oxethylated platinum-salt, had been prepared by the action of triethylamine on the bromethylated bromide:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N + H_2O = [(C_2H_5O)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

This equation involves the intervention of water in the reaction, which was obviously furnished by the imperfectly de-hydrated alcohol used in the experiments. In the anhydrous state, the bromethylated bromide and triethylamine scarcely act at 100°; between 120° and 130°, a reaction takes place, among the products of which, as yet very imperfectly examined, I was likewise unable to trace the presence of a phosphammonium-like compound. It can scarcely be doubted that this reaction gives rise to the formation of bromide of vinyl-triethylphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N = [(C_2H_3)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

Experimentally the question remains undecided.

The elegance and precision with which the bromethylated bromide fixes the elements of ammonia and of the monamines, very naturally suggested the idea of examining the deportment of this body under the influence of diamines and triamines. The results obtained in these experiments do not belong to this part of the inquiry. Suffice it to say for the present, that these substances attack the bromide with the utmost energy, giving rise to an almost unlimited number of polyatomic bases of a higher order, the

constitution of which, though complicated, is traceable in advance by the experience acquired in the simpler forms of reaction.

PHOSPHARSONIUM-COMPOUNDS.

There was no necessity for entering into a detailed examination of this class of compounds. I have in fact been satisfied to establish, by a few characteristic numbers, the existence of the phospharsonium-group.

Action of Triethylarsine on the Bromide of Bromethyl-triethylphosphonium.

On digesting the two substances in sealed tubes, the usual phenomena are observed. The saline mass which is formed yields, by treatment with oxide of silver *in the cold*, a powerfully alkaline solution containing the dihydrate of ethylene-hexethylphospharsonium,

$$C_{14}H_{36}PAsO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]'' \\ H_2\end{matrix}\right\}O_2.$$

It is thus obvious that the arsenic-base imitates the triethylphosphine in its deportment with the bromethylated bromide. The two substances simply combine to form the dibromide of the phospharsonium.

The alkaline solution of the hydrate of the phospharsonium exhibits the leading characters of this class of bases; I may therefore refer to the detailed account which I have given of the hydrate of the diphosphonium. The saline compounds likewise resemble those of the diphosphonium. The dichloride and the di-iodide were obtained in beautiful crystalline needles, exhibiting a marked tendency to form well-crystallized double salts. I have prepared the compounds of the dichloride with chloride of tin, bromide of zinc, trichloride of gold, and lastly, with dichloride of platinum. The latter compound was analysed in order to fix the composition of the series.

Platinum-salt.—The product of the reaction of triethylarsine upon the bromethylated bromide is treated with oxide of silver *in the cold*, and the alkaline solution thus obtained is saturated with hydrochloric acid, and precipitated with dichloride of platinum. An exceedingly pale yellowish, apparently amorphous precipitate of marked diphosphonic appearance is thrown down, almost insoluble in water, but dissolving in boiling concentrated hydrochloric acid. The hydrochloric solution deposits, on cooling, beautiful orange-red prisms, resembling the crystals of the corresponding diphosphonium-platinum-salt.

I. 0·4668 grm. of platinum-salt gave 0·3914 grm. of carbonic acid and 0·2003 grm. of water.

II. 0·4585 grm. of platinum-salt, fused with carbonate of sodium, gave 0·5460 grm. of chloride of silver. The platinum separated in this experiment was contaminated with arsenic.

The formula

$$C_{14}H_{34}PAsPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3As\end{matrix}\right]''Cl_2, 2PtCl_2$$

requires

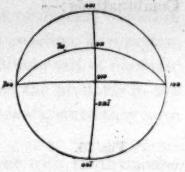
		Theory.	Experiment.	
			I.	II.
C_{14}	168	23·38	22·87	——
H_{34}	34	4·73	4·77	——
P	31	4·32	——	——
As	75	10·44	——	——
Pt_2	197·4	27·48	——	——
Cl_6	213	29·65	——	29·46
	718·4	100·00		

Quintino Sella has examined the crystals of the phospharsonium-platinum-salt. I append the results of his observations.

"System triclinic:—

$100, 010 = 81° 52'$; $100, 001 = 88° 14'$;
$010, 001 = 89\ 9$; $100, \bar{1}11 = 120\ 18$;
$010, \bar{1}11 = 64\ 4$.

Fig. 74.



Forms observed:—

100, 001, 010, 011, $\bar{1}11$, $02\bar{1}$ (Fig. 74).

Angles.		Calculated.	Observed.
100, 010	=	81° 52'	81° 52'
100, 001	=	88 14	88 14
100, 011	=	83 48	83 52
100, $02\bar{1}$	=	84 14	——
100, $\bar{1}11$	=	120 18	120 18
010, 001	=	89 9	89 9
010, 011	=	53 3	——
010, $02\bar{1}$	=	34 25	34 28
010, $\bar{1}11$	=	64 4	63 53
001, 011	=	36 6	——
001, $02\bar{1}$	=	123 34	123 38
001, $\bar{1}11$	=	46 54	46 37
011, $02\bar{1}$	=	87 29	——
011, $\bar{1}11$	=	36 30	——
$02\bar{1}$, $\bar{1}11$	=	91 15	——

According to NAUMANN:—

$a:b:c = 0{\cdot}8533:1{\cdot}1689:1$; $\alpha = 81°\,53'$; $\beta = 88°\,20'$; $\gamma = 90°\,36'$.

Forms observed:—

$\infty\bar{P}\infty$; $\infty\breve{P}\infty$; $0P$; $\breve{P}'\infty$; $2\breve{P}_{,}\infty$; P'.

According to WEISS:—

$a:b:c = 1:1{\cdot}1689:0{\cdot}8533$; $a\,o\,b = 98°\,7'$; $b\,o\,c = 90°\,36'$; $c\,o\,a = 91°\,40'$.

Forms observed:—

$a:\infty b:\infty c$; $\infty a:b:\infty c$; $\infty a:\infty b:c$; $\infty a:b:c$; $-a:b:c$; $\infty a:b:-2c$.

According to LEVY:—

$MT = 98°\,8'$; $TP = 91°\,46'$; $PM = 90°\,51'$.

$H:F:D = 0{\cdot}8533:1{\cdot}1689:1$.

Forms observed:—

M, T, P, d', e', $c^{\frac{1}{2}}$.

Combinations:—

100, 010, 001 (Fig. 75).

100, 010, 001; $\bar{1}11$ (Fig. 76).

100, 010, 001; $\bar{1}11$, $02\bar{1}$

100, 010, 001; $\bar{1}11$, $02\bar{1}$, 011 (Fig. 77).

Fig. 75.

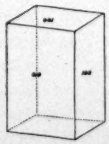


Fig. 76.

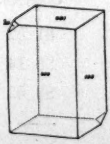


Fig. 77.

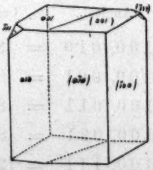
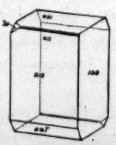


Fig. 78.



Cleavages 100 and 001: distinct and easily obtained. The cleavage is occasionally observed to take place during measuring, probably in consequence of the heat emanating from the face, which has to be brought close on account of the minuteness of the crystals.

Hemitropic crystals with the axis of hemitropy [001] (Fig. 78). It was possible to verify by measurement that the axis of hemitropy is really [001], and not a line perpendicular to one of the faces of the crystal."

The phospharsonium-compounds, and more especially the hydrate of the series, are far less stable than the corresponding terms of the diphosphonium-series.

If the product of the action of triethylarsine on the bromethylated monophosphonium be *boiled* with oxide of silver, instead of being treated in the cold, not a trace of the phospharsonium-compound is obtained. The caustic solution which is formed, yields, when saturated with hydrochloric acid and precipitated with dichloride of platinum, only the rather soluble octohedral crystals of the oxethylated triethylphosphonium.

The nature of this transformation is clearly exhibited when a solution of the hydrate of the phospharsonium, filtered off *in the cold* from the excess of oxide of silver, is submitted to ebullition. Immediately the clear liquid is rendered turbid from separated triethylarsine which becomes perceptible, moreover, by its powerful odour; the solution now contains the hydrate of oxethylated triethylphosphonium.

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3As + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O.$$

When the dibromide is boiled with the oxide of silver, a beautiful silver mirror is formed on the sides of the vessel, obviously in consequence of a partial oxidation of the liberated triethylarsine.

Some experiments were made to produce a diatomic compound containing phosphorus and antimony. I expected to form this body, the dibromide of a phosphostibonium, by the action of triethylstibine on the bromethylated bromide, so frequently mentioned in this paper. The two bodies react upon one another, but only after protracted digestion or exposure to a rather high temperature. The product of the reaction is complex, yielding a comparatively small quantity of a difficultly soluble platinum-salt of diatomic appearance. I have repeatedly modified the reaction, and analysed the products in the form of platinum-salts: I omit to quote the detail of these experiments, since they have failed to disentangle the difficulties of the reaction.

Some experiments upon the deportment of dibromide of ethylene with triethylarsine were more successful. The reaction between these two bodies had been selected as a subject of inquiry by Mr. W. Valentin, to whom I am indebted for valuable assistance at the earlier stages of these researches. Circumstances have subsequently prevented Mr. Valentin from carrying out his plan, and I have therefore to take upon myself the responsibility for the following statements. The results obtained in the examination of the arsenic-compounds are by no means absolutely connected with the study of the phosphorus-bases, nevertheless I may be permitted to lay them before the Society, together with the account of the corresponding reaction in the phosphorus-series.

MONARSONIUM-COMPOUNDS.

Action of Dibromide of Ethylene upon Triethylarsine.

The experience gathered during the examination of the phosphorus-bodies enabled me to establish the nature of this reaction by a comparatively small number of platinum-determinations.

Bromide of Bromethyl-triethylarsonium.—To avoid, as far as possible, the formation of the second product, a mixture of triethylarsine with a very large excess of dibromide of ethylene was digested in sealed tubes, at a temperature not exceeding 50° C. Notwithstanding this low temperature, the tubes invariably contained compressed gases. The

product of the reaction was treated with water, which extracted a soluble bromide from the ethylene-compound unacted upon. On evaporation, a beautiful bromide was left, which, being copiously soluble in boiling, and sparingly soluble in cold alcohol, could be readily recrystallized from absolute and even from common alcohol. In water this substance is excessively soluble; it is therefore scarcely crystallizable from an aqueous solution.

Analysis, as might have been expected, proved this salt to be the analogue of the bromethylated triethylphosphonium-salt. It contains

$$C_8 H_{19} As Br_2 = [(C_2 H_4 Br)(C_2 H_5)_3 As] Br.$$

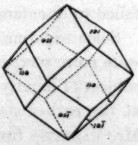
The bromide of bromethyl-triethylarsonium, the composition of which is sufficiently established by the analysis of the corresponding platinum-salt (see below), can be obtained in beautiful crystals. Their form—the rhombic dodecahedron—is identical with that of the corresponding bromethyl-triethylphosphonium-compound, which the crystals resemble also in their general habitus. I quote the following from SELLA'S examination:—

"System monometric.

Forms observed:—

1 1 0 (Fig. 79).

Fig. 79.



Angles.		Calculated.		Observed.	
		°	′	°	′
1 1 0, $\bar{1}$ 1 0	=	90	0	90	3
1 1 0, 1 0 1	=	60	0	60	0
1 1 0, 0 1 $\bar{1}$	=	60	0	60	8

No influence on polarized light."

Platinum-salt.—The solution of the previous salt, converted by treatment with chloride of silver into the corresponding chloride, yields with dichloride of platinum splendid needles of a double salt, difficultly soluble in cold and even in boiling water.

I. 0·9695 grm. of salt, treated with sulphuretted hydrogen, &c., gave 0·2040 grm. of platinum.

II. 1·2175 grm. of salt of a new preparation, analysed in the same manner, gave 0·2545 grm. of platinum.

III. 1·2815 grm. of salt of the last preparation gave 0·2715 grm. of platinum.

The formula

$$C_8 H_{19} Br As Pt Cl_3 = [(C_2 H_4 Br)(C_2 H_5)_3 As] Cl, Pt Cl_2$$

requires the following values:—

	Theory.		Experiment.		
			I.	II.	III.
1 equiv. of Arsonium . . .	270·0	56·82	——	——	——
1 equiv. of Platinum . . .	98·7	20·77	21·04	20·90	21·18
3 equivs. of Chlorine . . .	106·5	22·41	——	——	——
1 equiv. of Platinum-salt . .	475·2	100·00			

Compounds of Vinyl-triethylarsonium.

The bromide of bromethyl-triethylarsonium, like the corresponding phosphorus-compound, loses its latent bromine under the influence of oxide of silver. If the solution of the bromide be precipitated by an excess of nitrate of silver, one-half of the bromine separates as bromide of silver; the clear filtrate, mixed with ammonia, yields the second half of the bromine in the form of a dense precipitate. Nevertheless the reaction differs from that observed in the phosphorus-series. The bromide of the bromethylated phosphonium, as has been pointed out in a former part of this inquiry, is almost invariably converted into an oxethylated body, its transformation into a vinyl-compound being altogether exceptional. The bromide of the bromethylated arsonium, on the other hand, yields, as a rule, the vinyl-body of the series, the formation of an oxethylated compound taking place only under particular circumstances; in fact so rarely as to leave some doubt regarding the existence of this term of the series. The bromide of the bromethylated arsonium, treated with an excess of oxide of silver, yields a powerfully alkaline solution, the nature of which was determined by the analysis of the corresponding platinum-salt. Transformed into the chloride, and precipitated with dichloride of platinum, this solution yielded beautiful rather soluble octohedra.

I. 0·6312 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1570 grm. of platinum.

II. 0·6338 grm. of platinum-salt, analysed in the same manner, gave 0·1571 grm. of platinum.

III. 0·4345 grm. of platinum-salt gave 0·1093 grm. of platinum.

IV. 0·4135 grm. of platinum-salt gave 0·1025 grm. of platinum and 0·4525 grm. of chloride of silver.

V. 0·3370 grm. of platinum-salt gave 0·0843 grm. of platinum.

These numbers lead to the percentages of a vinyl-triethylarsonium-compound. The formula

$$C_8 H_{18} As Pt Cl_3 = [(C_2 H_3)(C_2 H_5)_3 As] Cl, Pt Cl_2$$

requires the following values:—

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
1 equiv. of Arsonium . .	189·0	47·94	——	——	——	——	——
1 equiv. of Platinum . .	98·7	25·05	24·87	24·79	25·15	24·78	25·02
3 equivs. of Chlorine . .	106·5	27·01	——	——	——	27·07	——
1 equiv. of Platinum-salt .	394·2	100·00					

Analyses I. and II. were made with the same specimen; analysis III. with a salt obtained in a new preparation; analysis IV. with a salt procured by precipitating the chloride left after the separation of the platinum in the form of sulphide in the previous analysis. For the first three experiments, the solution of the bromethylated arsonium-compound was gently heated with oxide of silver; for experiment V. the digestion had taken place in the cold.

The above numbers show that the transformation of the bromethylated compound ensues according to the following equation:—

$$[(C_2H_4Br)(C_2H_5)_3As]Br + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O = 2AgBr + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3As]\\H\end{matrix}\right\}O.$$

The idea suggested itself that the vinyl-compound obtained in this reaction might be a secondary product resulting from the decomposition of an oxethylated compound of limited stability formed in the first instance:

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3As]\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3As]\\H\end{matrix}\right\}O.$$

It was with the view of avoiding this decomposition, that the digestion was accomplished at the common temperature for experiment V.; the result, however, showed that even in this case the vinyl-compound was obtained.

Nevertheless the oxethylated body appears to exist. Under circumstances which were not sufficiently well observed at the time, the action of oxide of silver upon the bromide of the bromethylated triethylarsonium yielded an octohedral platinum-salt with the platinum percentage of the oxethylated compound.

0·6103 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1448 grm.=23·72 per cent. of platinum.

The formula

$$[(C_2H_5O)(C_2H_5)_3As]Cl, PtCl_2$$

requires 23·94 per cent. of platinum. I have not been able to reproduce this substance.

DIARSONIUM-COMPOUNDS.

Dibromide of Ethylene-hexethyl-diarsonium.—The bromide or chloride of the bromethylated arsonium is but slowly acted upon by triethylarsine at 100° C. Two days' digestion at that temperature had produced but a slight impression; at 150° the reaction is accomplished in two hours. The phenomena now to be recorded presented themselves in the succession repeatedly observed in the phosphorus-series. The dibromide

$$C_{14}H_{34}As_2Br_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2$$

yielded, when debrominated, the powerful alkali

$$C_{14}H_{36}As_2O_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6As_2]''\\H_2\end{matrix}\right\}O_2.$$

Treated with acids, this alkali produces a series of fine salts, amongst which the di-iodide deserves to be mentioned; it equals in beauty the corresponding diphosphonium-compound. I have fixed the composition of the series by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—Pale yellow crystalline precipitate, similar to the diphosphonium-compound, difficultly soluble in water, soluble in boiling concentrated hydrochloric acid, from which it crystallizes on cooling.

I. 0·8610 grm. of platinum-salt (not recrystallized), treated with sulphuretted hydrogen, &c., gave 0·2220 grm. of platinum.

II. 0·4885 grm. of platinum-salt (crystallized from hydrochloric acid), analysed in the same manner, gave 0·1265 grm. of platinum.

The formula

$$C_{14}H_{34}As_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]Cl_2, 2PtCl_2$$

requires the following values:—

	Theory.		Experiment.	
			I.	II.
1 equiv. of Diarsonium . . .	352·0	46·17	——	——
2 equivs. of Platinum	197·4	25·89	25·78	25·89
6 equivs. of Chlorine	213·0	27·94	——	——
1 equiv. of Platinum-salt . .	762·4	100·00		

Gold-salt.—The dichloride obtained after separating the platinum in the two preceding analyses by means of sulphuretted hydrogen, was precipitated by trichloride of gold. Yellow slightly crystalline precipitate, soluble in hydrochloric acid, from which it separates in golden-coloured plates.

0·5859 grm. of the salt, treated with sulphuretted hydrogen, &c., gave 0·2220 grm. of gold.

The formula

$$C_{14}H_{34}As_2Au_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]Cl_2, 2AuCl_3$$

requires

	Theory.		Experiment.
1 equiv. of Diarsonium . .	352	34·18	——
2 equivs. of Gold	394	38·25	37·89
8 equivs. of Chlorine . . .	284	27·57	——
1 equiv. of Gold-salt . . .	1030	100·00	

ARSAMMONIUM-COMPOUNDS.

Bromide of bromethylated triethylarsonium, as might have been expected, is capable of fixing ammonia and the monamines, giving rise to the formation of a series of compounds not less numerous than the bodies mentioned in the phosphammonium-series. I have been satisfied to study the action of ammonia upon the bromide.

Dibromide of Ethylene-triethylarsammonium.—Reaction complete in two hours at 100°. The product contains the bromide

$$C_8H_{22}AsNBr_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\,As\\H_3\quad\;N\end{matrix}\right]''Br_2,$$

which was converted, by means of oxide of silver, into the stable caustic base

$$C_8H_{24}AsNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3AsN]''\\H_2\end{matrix}\right\}O_2,$$

the composition of which was determined by the analysis of the platinum- and gold-salts.

Platinum-salt.—Needles difficultly soluble in boiling water, soluble in boiling concentrated hydrochloric acid, from which well-formed crystals are deposited.

0·4650 grm. of platinum-salt, treated with sulphuretted hydrogen, gave 0·1475 grm. of platinum.

The formula

$$C_8H_{22}AsNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\,As\\H_3\quad\;N\end{matrix}\right]''Cl_2,\,2\,PtCl_2$$

requires

	Theory.		Experiment.
1 equiv. of Arsammonium	207·0	33·53	——
2 equivs. of Platinum	197·4	31·97	31·72
6 equivs. of Chlorine	213·0	34·50	——
1 equiv. of Platinum-salt	617·4	100·00	

Gold-salt.—Yellow compound precipitated from the dichloride obtained in the previous platinum-determination, on adding a solution of trichloride of gold. Soluble in hydrochloric acid, deposited from this solution in golden-yellow plates.

0·3505 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0·1550 grm. of gold.

The values corresponding to the formula

$$C_8H_{22}AsNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\,As\\H_3\quad\;N\end{matrix}\right]''Cl_2,\,2\,AuCl_3$$

are

	Theory.		Experiment.
1 equiv. of Arsammonium . .	207	23·39	——
2 equivs. of Gold	394	44·52	44·22
8 equivs. of Chlorine	284	32·09	——
1 equiv. of Gold-salt	885	100·00	

I have also made a few experiments on the action of dibromide of ethylene upon triethylstibine. The reaction is slow, and required long-continued digestion at temperatures higher than that of boiling water. The tubes invariably contained much gas, and the product of the reaction proved to be an inattractively complex mixture of several compounds, many of them secondary, which by no means invited me to a more minute examination of this process. I omit to quote the few platinum- and chlorine-determinations which were made, since they do not admit of a simple interpretation.

In performing the experiments on the arsenic-bases I have been most ably assisted by my nephew, Dr. P. W. HOFMANN, to whom I express my best thanks for his active cooperation in this part of my inquiries.

The experiments carried out in the ethylene-series, develope clearly enough the nature of the diatomic bases, and their relation to the monatomic compounds. I have worked with predilection in this series because the accessibility and manageableness of the material greatly facilitate the unravelling of the often complicated reactions. There could be no doubt that the phenomena observed in the ethylene-series would likewise be reproduced in other homologous series. But as a general view of the nature of this group of bodies had been gained from the observations recorded in the preceding paragraphs, it appeared scarcely necessary to corroborate the results already obtained, by many further experiments, which would have been more or less mere repetitions of the former. Nevertheless I have, in certain cases, likewise drawn other groups into the circle of my observations. Some of the fragmentary results at which I thus arrived I will here briefly communicate.

METHYLENE-GROUP.

In another place* I have mentioned an experiment I had made in the hope of converting iodoform into iodide of carbon, which, however, had yielded nothing but the di-iodide of methylene, discovered not long previously by BOUTLEROW. As a considerable quantity of this interesting compound (the result of these experiments) was still at my disposal, I took the opportunity of examining more particularly its behaviour to triethylphosphine and the ammonias in general.

The methylenated derivatives of the phosphorus-bases will be more conveniently examined in connexion with another class of compounds, to which a special chapter of this inquiry must be devoted. I will therefore only briefly mention in this place, that I have succeeded in producing several of the bases belonging to the methylene-group. The members of this series present some peculiarities, distinguishing them in a marked manner from the corresponding ethylene-compounds.

PROPYLENE- AND AMYLENE-GROUPS.

The experiments in the propylene- and amylene-groups were instituted almost at the beginning of this investigation, at a time when the reaction between triethylphosphine and dibromide of ethylene had not yet been sufficiently disentangled. The removal of

* Journal of the Chemical Society, vol. xiii. p. 65.

the difficulties in the ethylene-series has naturally cooled my interest in the corresponding reactions of the propylene- and amylene-series, and hence this part of the investigation has been left incomplete.

Triethylphosphine is briskly attacked by the dibromides, both of propylene and amylene; the reactions, however, do not exhibit the welcome simplicity and smoothness which characterize those in the ethylene-series. Even in the propylene-compound, whether it be prepared from amylic alcohol or from iodide of allyl, we miss with regret the sharply defined characters of the corresponding ethylene-body; and in the butylene-, and still more in the amylene-series, these features become fainter and fainter.

When submitted to the action of the dibromides of propylene and amylene, triethylphosphine appears to undergo simultaneously two different sets of changes; the substances formed being partly direct products of the reaction, partly, and perhaps chiefly, indirect products. The diphosphonium-compounds of the propylene- and amylene-series are less stable than the ethylene-diphosphoniums, and are therefore always mixed with such products of decomposition as are formed in the ethylene-group only under the protracted influence of high temperatures. Under all circumstances, however, these dibromides give up the elements of hydrobromic acid, so that we have to eliminate a painfully small quantity of the searched-for products from an unprofitable mass of bromide of triethylphosphonium. In such cases the ordinary methods of separation no longer suffice, and we are compelled to resort to treatment with baryta, the real examination of the products beginning only after the liberated phosphorus-base has been removed by ether, and the bromide of barium decomposed by means of oxide of silver and carbonic acid. By this treatment, beautiful iodides and platinum-salts are obtained, which, however, have as yet been but partially and imperfectly investigated.

PHENYLENE-GROUP.

Unfortunately nothing but fruitless experiments. I had hoped to find in triethylphosphine a bridge between the phenyl- and the phenylene-series, but my expectations have not been realized. The analogy between the salts of bromethylated triethylphosphonium and of bromophenylated ammonium,

$$[(C_2H_4Br)(C_2H_5)_3P]Br,$$
$$[(C_6H_4Br)\quad H_3\quad N]Br,$$

is unmistakeable, and it remained to be seen whether triethylphosphine would attack the salts of bromophenylammonium according to the equation

$$[(C_6H_4Br)H_3N]Br+(C_2H_5)_3P=\left[(C_6H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\quad N\end{matrix}\right]''Br_2.$$

Unfortunately the mixture of the two bodies is not changed even after being heated for some time to 160°. No better result was obtained by substituting for the bromophenylamine, the corresponding iodinated base. A mixture of triethylphosphine and iodophenylamine, which had been kept for a day at 160°, yielded, on opening the tube,

an appreciable quantity of iodine, recognizable by silver-salts, but the decomposition was by no means complete. Hydriodic acid separated from the mixture an iodide which crystallized in long needles, and was found by analysis* to consist of iodide of iodophenylammonium. In the products of transformation of the phosphorus-base I was unable to trace the simple relations pointed out by theory.

BENZYLENE-GROUP.

In conclusion, I will mention a few experiments upon the mutual reaction between triethylphosphine and dichloride of benzylene. By this latter name I denote the compound, discovered by CAHOURS, which is produced by the action of pentachloride of phosphorus on bitter almond oil.

At ordinary temperatures, and even at 100°, the two compounds react but slowly upon each other; between 120° and 130°, however, especially in presence of alcohol, the change takes place with facility. The resulting crystalline mass, like that obtained in the corresponding experiments in the propylene- and amylene-series, consists chiefly of chloride of triethylphosphonium. After removing the phosphorus-base as completely as possible from the solution of the crystals, by the successive treatment with baryta, oxide of silver, and carbonic acid, there remained a strongly alkaline liquid, the nature of which I endeavoured to determine by the preparation of the iodide and platinum-salt. The liquid, saturated with hydriodic acid, yielded a well-crystallized iodide, which, however, was so soluble and deliquescent that no constant results could be obtained by its analysis. On the other hand, the somewhat sparingly soluble platinum-salt, which is precipitated in small laminæ on treating the solution of the chloride with dichloride of platinum, and which may be recrystallized without alteration from boiling water, yielded results agreeing with one another, although the products of different preparations were submitted to analysis.

I. 0·5979 grm. of platinum-salt gave 0·8166 grm. of carbonic acid and 0·2863 grm. of water.

II. 0·4580 grm. of platinum-salt gave 0·6290 grm. of carbonic acid and 0·2212 grm. of water.

III. 0·2413 grm. of platinum-salt gave 0·3310 grm. of carbonic acid and 0·1160 grm. of water.

IV. 0·6955 grm. of platinum-salt, decomposed by hydrosulphuric acid, &c., gave 0·1670 grm. of platinum.

V. 0·7594 grm. of platinum-salt, fused with carbonate of sodium, &c., gave 0·1810 grm. of platinum and 0·7875 grm. of chloride of silver.

* 0·2634 grm. of iodide, precipitated by nitrate of silver, gave 0·1778 grm. of iodide of silver = 36·48 per cent. of iodine.

The iodide of iodophenylammonium,

$$[(C_6H_4I)H_3N]I,$$

contains 36·60 per cent. of iodine, precipitable by nitrate of silver.

These numbers lead to the formula

$$C_{13}H_{22}P\,Pt\,Cl_3 = [(C_2H_5)_3(C_7H_7)P]\,Cl,\,Pt\,Cl_2,$$

which represents the platinum-salt of a phosphonium in which the fourth equivalent of hydrogen is replaced by the molecule C_7H_7 (probably benzyl, the radical of benzyl-alcohol).

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
C_{13}	156	37·66	37·25	37·46	37·41	——	——
H_{22}	22	5·31	5·32	5·36	5·34	——	——
P	31	7·49	——	——	——	——	——
Pt	98·7	23·83	——	——	——	23·87	23·83
Cl_3	106·5	25·71	——	——	——	——	25·65
	414·2	100·00					

The transformation of triethylphosphine under the influence of dichloride of benzylene, evidently takes place according to the following equation:

$$3[(C_2H_5)_3P] + C_7H_6Cl_2 + H_2O = [(C_2H_5)_3HP]Cl + [(C_2H_5)_3(C_7H_7)P]Cl + (C_2H_5)_3PO.$$

It may be that the formation of the triethyl-benzylphosphonium-compound is preceded by the production of an ephemeral diatomic base containing the radical C_7H_6,

$$2[(C_2H_5)_3P] + C_7H_6Cl_2 = \left[(C_7H_6)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,$$

which is subsequently decomposed under the joint influence of water and an excess of triethylphosphine. I have not, however, been able, experimentally, to trace this base. Moreover, a difference in the deportment of triethylphosphine with the compounds of ethylene and benzylene is readily intelligible, if we recollect that they are far from being analogous, bichloride of benzylene representing in the benzyl-group the diatomic derivatives which have been obtained from ethylic aldehyde.

The analysis of the benzyl-triethylphosphonium-platinum-salt concludes the experimental part of this section of my researches. The following Table gives at a glance the several groups of bodies examined in Parts II. and III. of this inquiry.

MONATOMIC COMPOUNDS.

PHOSPHORUS-GROUP.

MONOPHOSPHONIUM-SALTS.

Ethyl-series.

Salt of Tetrethylphosphonium . . . . . $[(C_2H_5)_4P]Br.$

Salt of Bromethyl-triethylphosphonium . . . . . $[(C_2H_4Br)(C_2H_5)_3P]Br.$

Salt of Chlorethyl-triethylphosphonium . . . . . $[(C_2H_4Cl)(C_2H_5)_3P]Br.$

Salt of Oxethyl-triethylphosphonium . . . . . $[(C_2H_4HO)(C_2H_5)_3P]Br.$

Salt of Vinyl-triethylphosphonium . . . . . $[(C_2H_3)(C_2H_5)_3P]Br.$

Ethyl-methyl-series.

Salt of Ethyl-trimethylphosphonium . . . . . $[(C_2H_5)(CH_3)_3P]Br$.

Salt of Bromethyl-trimethylphosphonium . . . . $[(C_2H_4Br)(CH_3)_3P]Br$.

Salt of Oxethyl-trimethylphosphonium . . . . . $[(C_2H_4HO)(CH_3)_3P]Br$.

Ethyl-benzyl-series.

Salt of Triethyl-benzylphosphonium . . . . . $[(C_2H_5)_3(C_7H_7)P]Br$.

ARSENIC-GROUP.

MONARSONIUM-SALTS.

Ethyl-series.

Salt of Tetrethylarsonium . . . . . $[(C_2H_5)_4As]Br$.

Salt of Bromethyl-triethylarsonium . . . . . $[(C_2H_4Br)(C_2H_5)_3As]Br$.

Salt of Vinyl-triethylarsonium . . . . . $[(C_2H_3)(C_2H_5)_3As]Br$.

DIATOMIC COMPOUNDS.

PHOSPHORUS-GROUP.

DIPHOSPHONIUM-SALTS.

Salt of Ethylene-hexethyldiphosphonium . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2$.

Salt of Ethylene-trimethyl-triethyldiphosphonium . . $\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2$.

Salt of Ethylene-hexmethyldiphosphonium . . . . $\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Br_2$.

ARSENIC-GROUP.

DIARSONIUM-SALTS.

Salt of Ethylene-hexethyldiarsonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2$.

PHOSPHORUS-NITROGEN-GROUP.

PHOSPHAMMONIUM-SALTS.

Salt of Ethylene-triethylphosphammonium . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\quad N\end{matrix}\right]''Br_2$.

Salt of Ethylene-methyl-triethylphosphammonium . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)H_2N\end{matrix}\right]''Br_2$.

Salt of Ethylene-tetrethylphosphammonium . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)H_2N\end{matrix}\right]''Br_2$.

Salt of Ethylene-pentethylphosphammonium . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_2HN\end{matrix}\right]''Br_2$.

Salt of Ethylene-trimethyl-triethylphosphammonium . $\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3N\end{matrix}\right]''Br_2$.

PHOSPHORUS-ARSENIC-GROUP.

PHOSPHARSONIUM-SALTS.

Salt of Ethylene-hexethylphospharsonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3As\end{matrix}\right]''Br_2$.

ARSENIC-NITROGEN-GROUP.

ARSAMMONIUM-SALTS.

Salt of Ethylene-triethylarsammonium . . . . . $\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\H_3\quad N\end{matrix}\right]''Cl_2$.

The experiments described in the preceding pages refer almost exclusively to the study of compounds belonging either to the phosphorus-series or to the phosphorus-nitrogen-series. Numerous analogous terms of the nitrogen-series, monatomic as well as diatomic, with which I have become acquainted in the course of my researches, have been left unnoticed in this memoir. I propose to examine the nitrogen-bodies in a special memoir; and I may here only remark that these substances, although differing in several points, nevertheless so closely imitate, in their general deportment, the corresponding terms of the phosphorus-series, that the picture which in the preceding pages I have endeavoured to delineate of the phosphorus-compounds, illustrates, in a great measure, the deportment of the nitrogen-bodies. We meet here with the peculiar case of the study of the phosphorus-group being in advance of that of the nitrogen-series, whilst generally the investigation of the phosphorus-compounds was taken in hand only after inquiries in the nitrogen-series had furnished the prototypes to be copied.

In conclusion, a few words about the further development of which the experiments described appear to be capable, and about the direction in which I propose to pursue the opened track.

Conceived in its simplest form, the transition from the series of monatomic to that of diatomic bases may be referred to the introduction of a monochlorinated or monobrominated alcohol-radical into the ammonium-nucleus, the chlorine or bromine thus inserted furnishing the point of attack for a second molecule of ammonia. If in bromide of ethylammonium we imagine 1 equiv. of hydrogen in ethyl replaced by bromine, we arrive at the bromide of bromethyl-ammonium, which is capable of fixing a second molecule of ammonia, and of being thus converted into the dibromide of ethylene-diammonium, the latent bromine becoming accessible to silver-salts,

$$[(C_2H_4Br)H_3N]Br+H_3N=[(C_2H_4)''H_6N_2]''Br_2.$$

The further elaboration of this reaction suggests two different methods for the construction of polyatomic bases of a higher order. In the first place, the number of ammonia-molecules to be incorporated in the new system may be increased by the gradually advancing bromination of the radical. By the further bromination of ethyl

in bromide of bromethyl-ammonium and the action of ammonia on the bodies thus produced, the following compounds might be generated:—

$$[(C_2H_3Br_2)H_3N]Br+2H_3N=[(C_2H_3)'''\ H_9\ N_3]''\ Br_3.$$
$$[(C_2H_2Br_3)H_3N]Br+3H_3N=[(C_2H_2)''''\ H_{12}N_4]''''\ Br_4.$$
$$[(C_2H\ Br_4)H_3N]Br+4H_3N=[(C_2H\ )''''\ H_{15}N_5]''''\ Br_5.$$
$$[(C_2Br_5)\quad H_3N]Br+5H_3N=[(C_2\quad)''''''\ H_{18}N_6]''''''\ Br_6.$$

Again, the fixation of the ammonia-molecules might be attempted, not by the progressive bromination of the ethyl, but by the accumulation of monobrominated ethyl-molecules in the ammonium-nucleus. The bromide of the di-bromethylammonium, when submitted to the action of ammonia, would thus yield the tribromide of a triammonium, the bromide of tri-bromethylammonium, the tetrabromide of a tetrammonium, and, lastly, the bromide of tetra-bromethylammonium, the pentabromide of a pentammonium.

$$[(C_2H_4Br)_2H_2N]Br+2H_3N=[(C_2H_4)''_2H_8\ N_3]'''\ Br_3.$$
$$[(C_2H_4Br)_3H\ N]Br+3H_3N=[(C_2H_4)''_3H_{10}N_4]''''\ Br_4.$$
$$[(C_2H_4Br)_4\quad N]Br+4H_3N=[(C_2H_4)''_4H_{12}N_5]''''\ Br_5.$$

As yet the bromination of the alcohol-bases presents some difficulty; appropriately selected reactions, however, will doubtless furnish these bodies. They will probably be obtained by indirect means, similar to those by which, years ago, I succeeded in preparing the chlorinated and brominated derivatives of phenylamine; or these substances may be generated by the action of pentachloride and pentabromide of phosphorus upon the oxethylated bases, a process which, from the few experiments recorded in this memoir, promises a rich harvest of results.

I have but faint hope that I may be able to trace these new paths to their goal; inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium- and tetrammonium-compounds begin to unfold themselves in unexpected variety.

I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr. Peter Griess has assisted me in the performance of my experiments on the phosphorus-bases. The truly philosophical spirit in which this talented chemist has accompanied me throughout the varying fortunes of this inquiry, will always be one of my most pleasing recollections.

XXV. *Researches on Foraminifera.—Fourth and concluding Series.*

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Received June 14,—Read June 14, 1860.

172. I HAVE now to bring to a close my account of the structure of those typical forms of Foraminifera which it has been my object to elucidate, by a description of four remarkable generic types; of which the first, *Polystomella*, has long been known, but has been hitherto very imperfectly comprehended; the second, *Calcarina*, has never been carefully studied; the third, *Tinoporus*, has only been very imperfectly known in one of its forms; and the fourth, *Carpenteria*, is altogether new. Each of these will be found to present features of interest peculiarly its own;—*Polystomella* being remarkable for the very symmetrical distribution of its canal-system, whose existence and whose relation to the multiple fossæ upon its surface have hitherto been altogether overlooked;—*Calcarina* being distinguished by the extraordinary development of its "intermediate" or rather "supplemental skeleton," and by the amplification of the canal-system for its nutrition;—*Tinoporus* presenting us with a type of structure that is intermediate between the *Rotaline* group (to which it is allied in the character of its individual chambers) and the *Orbitoline* (to which it approximates in its mode of growth), and that helps us greatly in the interpretation of the structure of the fossil *Orbitoides*;—and, lastly, *Carpenteria* furnishing us with a connecting link of the most striking significance between Foraminifera and Sponges.

Genus POLYSTOMELLA.

173. *History.*—Of the minute shells to which the generic name *Polystomella* is now assigned, one species, now known as *P. crispa*, seems to have early attracted the attention of conchological observers and collectors, on account both of its beauty and of the frequency of its occurrence; having been described and figured more than a century ago by PLANCUS and GUALTIERI, and adopted by LINNÆUS under the designation *Nautilus* into his 'Systema Naturæ.' By this designation it continued to be known from the time of LINNÆUS to that of LAMARCK; having been described and figured by WALKER, SOLDANI, FICHTEL and MOLL, MONTAGUE, DILLWYN, and many other writers of the latter part of the last and the early part of the present century. Its dissimilarity to *Nautilus* was first clearly pointed out in 1822 by LAMARCK; who conferred upon it the generic distinction *Polystomella*, apparently under the impression that the numerous pits on its surface are really multiple mouths of passages leading directly to its chambered cavity. His definition of the genus, contained in the First Edition of his 'Animaux sans Vertèbres' (tom. vii. p. 625), is as follows:—"Coquille discoïde, multiloculaire, à tours

contigus, non apparens au-dehors, et rayonnée a l'extérieur par des sillons ou des côtes qui traversent la direction des tours. Ouverture composée de plusieurs trous diversement disposés." The genus was soon afterwards adopted by M. D'ORBIGNY in his first systematic classification of Foraminifera*; and he seems also to have adopted LAMARCK'S idea of the structure of this type, which he defines as follows†:—"Les Polystomelles se distinguent de tous les genres de Nautiloidées par ce caractère singulier, que les ouvertures du bord de la dernière loge reparaissent en fossettes, plus ou moins allongées, sur toutes les autres; les dernières seulement ouvertes, les autres fermées. Il en résulte qu'extérieurement ce genre se distingue de suite par ce grand nombre de petits excavations transversales, qu'on remarque sur toutes les espèces." He elsewhere adds to this description: "L'animal fait sortir des filamens non seulement par des ouvertures du dessus de la dernière loge, mais encore par des pores des côtés des dernières"‡. The same definition is more concisely repeated by M. D'ORBIGNY in his latest publication on the subject, notwithstanding that the true structure of *Polystomella crispa* had in the mean time been elucidated by Professor WILLIAMSON in his admirable memoir on that species; the genus *Polystomella* being still defined (in the 'Cours Élémentaire de Paléontologie et de Géologie Stratigraphiques,' tom. ii. p. 197) "Coquille nautiloïde, pourvue de nombreuses ouvertures sur la dernière loge et sur les côtés de la coquille; une cavité simple au loges."

174. I have already referred, in my General Introduction, to the elaborate inquiry of Professor WILLIAMSON into the organization of *Polystomella crispa*§, as having not only established several important facts in regard to its minute structure, but as having furnished the starting-point for all future investigations of the same kind: it now becomes necessary that I should somewhat fully recapitulate the most important features of his description, in order that it may be seen in what points my own inquiries upon a more developed form of the same group have evolved results supplementary to his. To the accuracy of his descriptions I can bear the fullest testimony; having not only had the opportunity, through the kindness of Professor WILLIAMSON, of examining the preparations still in his possession both of the shell and of the animal of *Polystomella crispa*, but having carried out an independent investigation upon specimens collected by myself.

175. On the exterior of each of the segmental divisions of the shell of *P. crispa*, strong transverse crenulations present themselves, which are deepest near the convex margin of the preceding septal band, where they terminate somewhat abruptly, and usually disappear before reaching the concave margin of the subsequently-formed chamber. The depressions between the elevated ridges, which are the "fossettes" of M. D'ORBIGNY, often present the appearance of orifices; but this appearance is fallacious, since at no

* "Tableau Méthodique de la Classe des Céphalopodes," in Annales des Sciences Naturelles, 1826.

† Voyage dans l'Amérique Méridionale, tom. v. p. 29.

‡ Foraminifères Fossiles de Vienna, p. 121.

§ Transactions of the Microscopical Society, First Series, vol. ii. p. 159.

period in the growth of the shell is there any passage through these "fossettes" to the cavity of the chamber,—the only communication possessed by any chamber either with contiguous chambers or (in the case of the outermost chamber alone) with the exterior, being afforded by a variable number of minute orifices (corresponding with the septal pores of *Peneroplis*) which are to be found near the inner margin of each septal plane, close to its junction with the preceding convolution. Corresponding to the elevated ridges of the crenulations, we find a series of grooves on the internal surface, which shallow towards the anterior or concave margin of each segment, and deepen towards the posterior or convex margin; and for a short distance from the posterior septum each groove is converted into a tube by a narrow lamella given off internally from the septum. These tubes, however, establish no communication between the contiguous chambers; for they are *culs de sac*, closed-in by the lamella of the septum which formed the boundary of the previously-formed chamber. In the living state they are occupied (as can be shown by examination of the decalcified body) by a set of processes of sarcode, which extend backwards for a short distance from both the outer or lateral margins of each segment of the sarcode-body, and then terminate abruptly. From the neighbourhood of the inner arch of each segment, on the other hand, there proceeds a series of threads of sarcode much slenderer than the "retral processes" just described, which unite each segment to the two contiguous segments before and behind, passing through the row of pores already mentioned as visible along the inner margin of the septum. The shell is described by Professor WILLIAMSON as "crowded with myriads of minute foramina," and as also covered over with small pointed tubercles, which, from the rounded forms of their bases, and their great transparency, may be easily mistaken for apertures in the shell, especially in the "fossettes," where these tubercles are often very large. He further pointed out that the umbilical region is occupied by a solid mass of shelly substance, into which the decalcified animal does not appear to extend, and the surface of which is often marked with small depressed pits, the orifices of vertical internal passages, through which pseudopodia are probably protruded.

176. It is obvious from the foregoing account that if *Polystomella crispa* is to be taken as the type of the genus, the generic definition given by M. D'ORBIGNY is based on an entire misapprehension of its true structure; the only considerable departure from the general type of *Hélicostègue* structure being the substitution of a series of isolated pores for the ordinary single orifice of communication between the successive chambers (a difference which in the case of *Peneroplis* and *Dendritina* we have seen to have not even a specific value), and the supposed lateral orifices having no real existence.

177. Subsequently to Professor WILLIAMSON'S memoir, an elaborate account of the characters of the genus *Polystomella*, and especially of a species designated *P. strigilata* (which seems to me only one of the multiform varieties of *P. crispa*), has been given by Professor MAX SCHULTZE, in the excellent treatise 'Über den Organismus der Polythalamien,' to which I have already referred. He had the advantage of being able to study this species in the living state; and he has thus been enabled to give a beautiful

figure, not merely of the shell, but also of the pseudopodia protruded from various parts of its surface; as well as to make preparations of the sarcode-body of the animal, by dissolving away the shell in dilute acid. He does not seem, however, to have had the advantage of a full knowledge of Professor WILLIAMSON'S memoir; his acquaintance with it being apparently limited to the abstract of it contained in 'L'Institut' (No. 787); and I find in his description of the shell a confirmation of the belief I have already had occasion to express, that he has not availed himself as fully as is desirable of the mode of examining the intimate structure of these minute objects by the preparation of very thin sections. In every point, in fact, in which he differs from Professor WILLIAMSON, I am satisfied that the truth lies with the latter; and this not merely on account of the entire coincidence between the results of my own inquiries into the structure of *Polystomella crispa* and those of my accomplished predecessor, but also because our views are in every respect borne out by the structure of the much larger and more highly developed form of *Polystomella* which I am presently to describe. One point in Professor SCHULTZE'S description, however, requires special notice. He states that each of the crenulated prominences which are seen on the surface of the lateral walls of the chambers is traversed longitudinally by a wedge-shaped fissure, that is narrowest as it approaches the septal band, near which it penetrates the cavity of the chamber, whilst it becomes shallower as it widens out at the part where the crenulation merges in the smooth wall of the shell. I expect to be able to show that the supposed "fissures" of Professor SCHULTZE no more communicate with the cavity of the chambers, than do the "fossettes" of M. D'ORBIGNY; but that they are really the outlets of the canal-system, whose existence in *Polystomella* has not been discovered either by Prof. SCHULTZE or by Prof. WILLIAMSON, but which attains an extraordinary development in the type which has specially fallen under my observation.

178. The specimens of *Polystomella*, of which I have now to give an account, were chiefly collected by Mr. JUKES in his Australian dredgings; I have met with the same form, however, in Mr. CUMING'S Philippine collection; and I have reason to believe it to be generally diffused through the Indian and Polynesian seas. It seems to be the *P. craticulata* of FICHTEL and MOLL. The empty shells are occasionally the subjects of that very curious infiltration of silicate of iron, to which attention was first directed by Professor EHRENBERG as a peculiar mode of fossilization of Foraminifera,—causing internal "casts" of their chambers to be preserved long after their shells have been destroyed,—in his memoir 'Über den Gruensand und seine Erläuterung des organischen Lebens"*, and which was soon afterwards shown by Professor BAILEY† to be taking place at the present time over certain parts of the ocean-bottom. I have recently been enabled, through the kindness of Mr. W. K. PARKER, to examine a number of most perfect and beautiful "casts" which he has obtained, not merely of fragments, but of the entire animal of this type of *Polystomella*, by treating with dilute acid shells which

* Abhandlungen der Königl. Akad. der Wissenschaften, Berlin, 1855.

† Quarterly Journal of Microscopical Science, vol. v. p. 83.

have been thus infiltrated. These casts represent not merely the segments of the sarcode-body with their connecting stolons, but also those prolongations of the body which occupied the canal-system; and as they preserve with the greatest exactitude the natural forms and relative positions of these parts, they really afford more precise and satisfactory information than that which could have been derived from an examination of the sarcode-body of the animal itself, since its softness and friability are such as greatly to interfere with the due appreciation of its characters, when it is deprived of the support afforded by the shell.

179. *External Characters.*—This type of *Polystomella* (Plate XVII. fig. 1, *a*, *b*) is distinguished from the others already noticed, not only by its comparatively large dimensions,—the diameter of some of the specimens in my possession exceeding one-sixth of an inch,—but by the considerable proportion of its two lateral surfaces occupied by that solid calcareous nucleus which is confined in other species to the umbilical region. The diameter of this nucleus is usually about three-fifths of the whole diameter of the specimen; so that it covers and conceals all the earlier convolutions, meeting at its outer margin the chambers of the last formed whorl (as is made evident by vertical sections, Plate XVII. fig. 2), which are consequently the only chambers that show themselves externally, although the last formed whorl does not itself extend far over the preceding. I have not unfrequently found this central nucleus, however, to be sufficiently transparent (after its surface has been cleaned by a short immersion in dilute acid) to allow of the inner convolutions being discerned through it, when the microscope is focused down to their surface, and a strong light is directed upon this; and it then becomes obvious that, if the solid nucleus were removed, the form of the shell would be bi-concave instead of bi-convex, the thickness of each whorl (*i. e.* the distance between its two lateral surfaces) being greater than that of the preceding, and the later whorls not extending themselves over those previously formed. The septa are marked externally (as in most other Foraminifera of the nautiloid type) by bands which indicate their junction with the outer walls of the chambers: these bands are meridional (so to speak) in their direction, extending from the margin of the nucleus on one side to that of the nucleus on the other side; they are not usually (in adult specimens at least) either elevated above or depressed below the surface of the walls of the chambers on either side of them; but they are distinguished by their difference of texture, their substance being much more transparent and glistening than that of which those walls are composed.

180. The surface of the central nucleus is marked at pretty regular intervals with minute punctations (fig. 1, *b*), each of which occupies the centre of a little dimple or depression; and rows of similar punctations are very commonly seen to extend from the nucleus on either side, in a direction corresponding to that of the septal bands (fig. 1, *a*), two such rows usually intervening between each septal band and that which precedes or follows it (Plate XVIII. fig. 1, *hh*, *h'h'*). In the older portion of the last formed whorl, it is sometimes to be observed that these punctations with their surrounding dimples

constitute the only interruption to the general uniformity of the surface, the septal bands not being clearly distinguishable; and this disposition is commonly found to prevail on the surface of the inner whorls, when it is exposed by the removal of the outer (*ii'*, *ii'*). In the newer portion of the last formed whorl, on the other hand, we may observe that instead of each punctation having a separate dimple of its own, the corresponding punctations of the two rows lie in a succession of furrows that pass transversely between the septa (*gg'*, *gg'*). In the most recently formed portions of specimens that have not attained their full growth, we find these furrows to be deeper towards the posterior than towards the anterior margin of each interseptal space; and in the deepest portion of each of these furrows, which obviously correspond with the "fossettes" of *P. crispa* (although much less pronounced), a minute punctation may be brought into view by careful examination,—a corresponding row of punctations being also traceable on the other side of the septum*. These varieties of superficial aspect may present themselves on different parts of one and the same specimen; and it will appear from the explanations which I shall presently have to furnish, that they are occasioned by differences in the degree in which the proper external wall of the chambers is thickened by an exogenous deposit upon its surface, continuous with that of which the central nucleus is composed (¶ 185).

181. *Internal Structure.*—By the fortunate contingency already adverted to, I have been enabled to study the internal structure of this remarkable type, not merely by examining thin sections of the shell taken in various directions, and by comparing the appearances they present with those obtained by laying open its interior by fracture; but also by submitting to microscopic examination siliceous "casts" of its cavities and channels, which appear to represent with the utmost fidelity the forms and connexions of the various parts of the sarcode-body which occupied those cavities and channels in the living state of this organism. Between the results of these two modes of study I have found the conformity to be so exact, that the account of the structure of the animal which I should have given from examination of the shell alone, has not needed to be modified in the slightest particular by the information more recently furnished by these "casts;" and, in point of fact, the ideal representation in Plate XVIII. fig. 1, which was entirely based on the former source of information, has not needed the least alteration to bring it into accordance with the exact delineations of the latter class of objects which are given in figs. 12, 13†.

182. In the general shape and proportions of its segments, this type of *Polystomella*

* In order to distinguish the orifices of these punctations, it is advantageous to remove from the surface of the shell that opacity which it derives from abrasion, and to get rid of the fine particles of calcareous matter which often choke up and obscure its pores. This is readily effected by immersing it for a short time in water so slightly acidulated with nitric or hydrochloric acid as only to exert a very feeble degree of solvent power.

† I think it well to state this circumstance, as it may increase the confidence accorded to my descriptions of other types, of which the shells alone have been submitted to examination.

differs remarkably from most of the other nautiloid Foraminifera; the breadth of each of the later whorls being many times exceeded by what may be termed its thickness, that is, by the distance between its two lateral surfaces. Thus the segments come to have somewhat of the form and arrangement which the carpels of an orange would exhibit, if, instead of lying in a single circle round a central axis, they were disposed in a succession of whorls, with a progressive increase in their dimensions. This comparison may be conveniently carried a little further. For as each carpel of the orange has its own investing membrane, so that the partitions between the adjacent carpels are double, so each segment of *Polystomella* has its own proper shelly investment, causing the septa which separate the adjacent segments to be double,—as was originally pointed out by Professor WILLIAMSON, and as I have shown to be the case also in the higher types of Foraminifera generally. But further, as the separate carpels of the orange are collectively invested by a general integument, which also to a certain degree dips down between them, and which fills up what would otherwise be void spaces about the two poles of the spheroid, so shall we find that the proper walls of the spirally arranged segments of *Polystomella* are strengthened and consolidated by a secondary calcareous deposit upon their external surface, corresponding to that "intermediate skeleton," of which less developed examples have already been furnished by *Cycloclypeus*, *Heterostegina*, *Operculina*, and *Amphistegina*,—its most distinctive peculiarity in *Polystomella* being its extraordinary thickness on the two lateral surfaces of all but the last formed whorl.

183. The spire of *Polystomella*, like that of other nautiloid Foraminifera, commences in a central cell, the dimensions of which are extremely variable; the difference between the extremes of its size being, in fact, not less remarkable than that which I have shown to present itself in *Orbitolites* (First Series, ¶ 44). Thus in Plate XVII. fig. 3, which represents a section of the five inner whorls of a full-grown specimen, taken through the equatorial plane, we trace a progressive diminution in the size of the chambers as we approach the central cell, which is itself no larger than the chambers in nearest proximity to it. In fig. 4, on the other hand, which represents a corresponding section of the inner portion of another specimen, drawn under the same magnifying power, we see that not only is the size of the earlier whorls and of their component chambers considerably greater, but that the central cell alone occupies about the same space as the first $2\frac{1}{2}$ whorls of the specimen represented in fig. 3. The average seems to be intermediate between these two extremes. The breadth of the successive whorls increases much more gradually than in most other nautiloid Foraminifera, in this respect resembling *Nummulites* rather than the recent forms described in former memoirs; and there is no tendency whatever, even in the oldest and most developed specimens, to that rapid opening-out of the spire, which we have seen to be so marked a feature of the older specimens of *Heterostegina*, *Peneroplis*, *Operculina*, and *Amphistegina*. The largest number of whorls I have met with in any individual (that, namely, to be counted in the specimen whose inner portion is represented in fig. 3) is *eleven*:

the earlier four or five of these completely invest the preceding, their chambers extending on either side to the centre of the spire, as is partly shown in the vertical section (Plate XVII. fig. 2); but as new whorls are added around these, the chambers cease to be thus prolonged over the preceding whorls, which would consequently be apparent externally if not concealed by the nucleus. The distance between the successive septa remains nearly the same after the spire has made two or three turns; and thus the size of the segments, as seen in an equatorial section, remains pretty much the same throughout all the later growth of the shell, while the number of chambers in the successive convolutions increases nearly in proportion to the length of those convolutions.

184. In these particulars, therefore, *Polystomella* corresponds rather with the *Cyclostègue* than with the ordinary *Hélicostègue* Foraminifera; and this correspondence is further borne out by the existence of an obvious relation in the position of the chambers of successive whorls, which exists in the former, but which cannot be traced in those forms of the latter to which our attention has hitherto been directed. It has been shown that, in *Orbitolites* and *Cycloclypeus*, the chambers of each concentric zone normally alternate in position with those of the zones which adjoin it internally and externally (¶¶ 17, 18, 100); and that this relation arises out of the mode of their communication with each other. In *Peneroplis*, *Operculina*, and *Amphistegina*, on the other hand, the position of the chambers of each successive whorl appears to be perfectly independent of that of the chambers in the whorl which preceded it. Now in the *Polystomella* whose structure we are considering, such an alternating arrangement appears to be the normal one, as is shown in the relation of the chambers *b*, *b*, Plate XVII. fig. 8, to *a*, *a*, and *c*, *c*; so that lines drawn from the centre of the spire through the septa of one convolution would pass through the middle of the chambers of the next, and would again meet the septa of the convolution beyond. This arrangement is shown in Plate XVII. fig. 7, as it presents itself in an actual section, and more diagrammatically in Plate XVIII. fig. 1; in both the vertical plane of section lays open the chambers a, a^1, a^2, whilst it traverses the septa b, b^1, b^2, b^3 of the alternating whorls. It is, however, by no means constant; being very liable to be disturbed by that *interpolation* of additional chambers, which is required for the augmentation of their number in successive whorls. We shall presently see (¶ 189) that although this relation does not depend, as in *Orbitolites* and *Cycloclypeus*, upon direct communications between the chambers of successive rows, it is manifestly connected with the peculiar disposition of the canal-system, which here acquires a remarkable development and importance.

185. Although, however, there is but little progressive increase in the dimensions of the successive chambers, and of the segments of the sarcode-body which occupy them, as seen in sections taken through the equatorial plane, it is made obvious by sections made at right angles to this (Plate XVII. fig. 2), that a rapid augmentation takes place in what may be termed the meridional direction; the distance between the two lateral surfaces of each whorl being considerably greater than between those of the preceding, so that the chambered portion of the shell progressively increases in thickness from the centre

towards the circumference. The conical hollow thus left on each side in the central portion of the shell, is entirely filled up by the solid nucleus already adverted to: the calcareous deposit, however, of which the nucleus is composed is by no means limited to it, but extends over the whole outer surface of each whorl, except where (in well-preserved specimens) the portion last formed is as yet unconsolidated by it. For a careful examination of sections taken in different directions, makes it clear that whilst the internal portion of the spiral lamina that forms the outer wall of each chamber is continuous with the nearest lamella of the adjacent septum on either side (Plate XVII. fig. 10), the substance of the external portion is no less continuous with that of the calcareous nucleus. The additional deposit is obviously homologous with that which forms the "intermediate skeleton" in *Cycloclypeus* (¶ 99), though less differentiated from the proper walls of the chambers than we have seen it to be in that type, or than we shall find it to be in *Calcarina* (¶ 202). The whole thickness of the spiral lamina is generally traversed by minute tubuli, passing in a radial direction from one surface towards the other; but these have by no means either the closeness or the regularity which distinguishes the tubular structure in *Cycloclypeus* and *Operculina*, and the shell-substance is in many parts so destitute of tubuli as to be of almost glassy transparence. The furrowing of the external surface (¶ 180) is seen in vertical sections (Plate XVII. fig. 2) not to be produced by mere superficial excavations, but to proceed from a plicated arrangement of the spiral lamina; and this is related to the prolongation of the posterior margin of each segment into a series of "retral processes" (Plate XVIII. fig. 12, *a*), corresponding to those described by Professor WILLIAMSON in *Polystomella crispa* (¶ 175). They are, however, much less elongated in this type, simply giving a crenulated margin to that angle of the segment, which contrasts remarkably with the smooth unbroken aspect of its anterior border *b*, *b'*. The spiral lamina which forms the outer wall of the chamber, being modelled (so to speak) upon the surface of these retral processes, presents internally a corresponding series of grooves, which are deepest towards the posterior margin, and become rapidly shallower in passing towards the anterior margin, of each chamber, as is shown at *a*, a^1, a^2, figs. 1 and 11, Plate XVIII.: these grooves are not, however, as in *P. crispa*, completed into tubes for part of their length by an additional lamella of shell given off from the septum (¶ 175); but they are sometimes shown, in sections which happen to traverse them (Plate XVII. fig. 10), to be extended into cæcal prolongations (*a*, *a*) by backward inflexions of the septa at their junction with the spiral lamina.

186. The communication between the successive segments of the same whorl is established by a number of minute processes or *stolons* of sarcode (*c*, figs. 12, 13, Plate XVIII.), which pass at regular intervals between their internal margins through a series of pores which can be distinguished along the inner border of each septum (fig. 1, *c*, *c'*, *c''*) close to its junction with the preceding convolution. I have not detected in any instance, either in sections of the shell, or in the siliceous casts which so exactly represent the sarcode-body, any other communications between the chambers or their contained seg-

ments; and I am therefore strongly disposed to believe that Professor MAX. SCHULTZE must have been misled by appearances when he stated (*op. cit.* p. 65) that various other parts of the septal plane are marked by similar pores,—more particularly as his figures of the decalcified body do not show that any other threads or stolons of sarcode pass from one of its segments to another, than those just described.

187. So far, then, the structure of this comparatively gigantic type of *Polystomella* accords very closely with that of the more delicate species so well described by Professor WILLIAMSON. I have now, however, to give an account of a remarkable feature in its organization, namely, its highly developed *canal-system*; which, though not entirely wanting in *P. crispa*, is so imperfectly presented there, that Professor WILLIAMSON may well be excused for having overlooked it, especially when it is borne in mind that at that period the existence of such a system in Foraminifera was altogether unknown. The general arrangement of this canal-system may be most readily apprehended from an examination of the delineations of the internal casts given in Plate XVIII. figs. 12, 13; for the infiltrating substance which has penetrated the chambers has also found its way not only into the main trunks, but also into the minute ramifications of this system, and has thus given just that representation of their distribution and relations, which is afforded in regard to the blood-vessels of the higher animals by a well-injected and clearly dissected anatomical preparation. We observe, in the first place, that in each of what may be termed the two polar regions of the spheroidal body, there is a continuous spiral canal (fig. 12, d, d^1, d^2), which overlies the extremities of the segments. These two spiral canals (which, although so widely removed from each other, are obviously homologous with the two spiral canals of *Operculina*, ¶ 159) communicate with each other by a very regularly disposed series of canals which pass in a meridional direction between the adjacent external margins of the segments (e, e^1, e^2). And each of these meridional canals gives off, in its course from one polar region to the other, a uniform succession of pairs of short passages (f, f^1, f^2) that diverge from each other widely, one series inclining backwards over the uniform anterior margin of the segment next behind it, whilst the other series passes forwards in the intervals between the "retral processes" of the segment next in front of it. The passages which thus diverge from the meridional canals of the outer whorl speedily debouch at its surface; but if we examine into the termination of those appertaining to the inner whorls (which is best seen in such fragments as the one represented in fig. 13), we find that they become continuous with the stolons of the whorl which surrounds them, as is shown at c, c', fig. 12. Further, it may be perceived that each of the meridional canals receives branches from the canal-system of the segment internal to it; this point, however, can be more clearly made out in sections of the shell.

188. The spiral canals are frequently brought into view for part of their course, by sections of the shell that pass through it in a direction parallel to the equatorial plane, but at no great distance from one of the lateral surfaces. Such a section, passing over the chambers of the inner whorls, is shown in Plate XVII. fig. 5; where we see the

spiral canal giving off the meridional canals, and these again sending off their diverging branches. Towards its centre, the spiral canal communicates with an irregular set of *lacunæ*, which are excavated in the solid nucleus. In Plate XVII. fig. 6, are shown portions of two whorls (*a*, *a*, and *b*, *b*) of the spiral canal, as shown in a section passing near the lateral surface of the outer convolution; proceeding from the outer side of these, in like manner, we see the meridional canals (*c*, *c*, *c'*, *c'*, *c'*) with their first pairs of diverging branches (see also fig. 12); whilst another set of canals (*d*, *d*, *d*) is seen to proceed from the inner side of the spiral canals, tending more or less obliquely towards the lateral surface; and the portion of the section which passes through the solid calcareous nucleus is seen to be perforated by numerous apertures (*e*, *e*) of corresponding diameter, disposed at pretty regular intervals. The relation of these to the canal-system is clearly evidenced by vertical sections, such as those represented in figs. 2 and 11; in which we see at *a*, *a*, the orifices of the spiral canals transversely or obliquely divided, and their connexion with the meridional canals *b*, *b*; and which further show that the solid calcareous nucleus is itself traversed by straight canals, *c*, *c*, *c*, which spring from the successive convolutions of the spiral canal, and pass directly, without branching or inosculation, to the external surface. That this remarkable portion of the canal-system does not fully show itself in the "casts" represented in Plate XVIII. fig. 12, is easily understood, when it is remembered that the whole substance traversed by the straight canals having been removed, their long and slender casts would be left entirely without support; and the points at which these have been broken off from the cast of the spiral canal are in fact to be seen on a careful examination, as there represented.

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189. It is shown by the comparison of vertical and horizontal sections of the shell with fragments obtained by fracture (Plate XVII. figs. 2, 7, 10, Plate XVIII. fig. 11), that the meridional canals are in reality spaces left by the divergence of the two layers of which each septum is composed, in the immediate neighbourhood of its junction with the spiral lamina which constitutes the external wall of the chamber (Plate XVII. fig. 7, *c*, and fig. 10, *b*; Plate XVIII. fig. 11, *b*, *b*); and that they are thus homologous with the arches of the interseptal system of canals that connect together the spiral canals of *Operculina* (¶ 157),—presenting, however, a much greater uniformity and constancy in their disposition. The diverging branches given off from these (Plate XVII. fig. 8, *d*, d^1, d^2) consequently pass at once into the spiral lamina, through which they run obliquely towards the external surface of the convolution, usually increasing in diameter as they proceed. The divergence of the branches of each meridional canal causes those proceeding from adjacent canals to approach one another; and when the spiral lamina has attained its full development, they not unfrequently open at its surface into the same depression, this being midway between the septa from which they respectively sprang; and it appears to be from the correspondence of these junctions with the intervals between the segments of the succeeding whorls (as seen at *e*, *e'*), that the alternating arrangement of the chambers of consecutive whorls arises, of which

mention has already been made (¶ 184), the prolongations of sarcode which occupy the diverging branches there passing into the stolons which connect the adjacent segments. It will be easily understood, however, that the position of the external orifices of these diverging branches will depend upon the thickness of the spiral lamina which they have to traverse before gaining its surface. In the newest portion of a shell which has not yet attained its full growth, we find that lamina comparatively thin; its surface is distinctly marked by the septal bands (Plate XVIII. fig. 1, *gg'*, *gg'*); and the external walls of the chambers present an alternation of ridges and furrows, passing directly across from one septal band to another,—the ridges corresponding to the grooves of the internal surface that receive the "retral processes" (¶ 185), and the furrows with the internal ridges that separate these grooves. Into these furrows, which represent the deeper "fossettes" of *P. crispa*, the diverging pairs of branches from each meridional canal open by minute pores on either side of the septal band, as is shown in fig. 1, and as will be readily understood from the relation of the parts as displayed in fig. 12. The subsequent formation of a calcareous deposit, continuous with that which solidifies the umbilical portion of the shell, upon the external surface of the spiral lamina (¶ 185), renders the septal bands less distinct, and obliterates the ridges and furrows of the intervening surface, as shown in the portion *h h'* of fig. 1; and at the same time it carries the orifices of the diverging branches from the neighbourhood of the septa into closer proximity with those of the branches proceeding from the adjacent meridional canals. As the diverging branches enlarge greatly in diameter with their augmentation in length, their superficial orifices become more and more conspicuous; each is surrounded by a little pit or depression of its own (fig. 1, *ii'*, *ii'*); and the rows of these depressions, when the spiral lamina has acquired its full thickness, constitute the only markings which it presents, the septal bands being completely obliterated,—as is best seen on the surface of one of the interior whorls, exposed by the removal of that which covered it. It is obvious, therefore, that these depressions, which are related only to the distribution of the canal-system, are essentially different in character and position from the "fossettes" of *P. crispa*, which intervene between the ridges that cover-in the retral processes; but they have this in common, that the orifices of the diverging branches are to be found in both of them; and the removal of the superficial portion of the spiral lamina, even when thickest (which may easily be accomplished by the assistance of dilute acid), brings back these orifices, in *P. craticulata*, to the immediate neighbourhood of the septal bands, which then again become apparent*.

190. The meridional canals are further connected with the older and more internal portions of the organism, as well as with the newer and more superficial; this connexion being established by a series of branches that pass between the two layers of the septa

* This arrangement of the orifices of the diverging branches of the meridional canals is beautifully shown (as Mr. W. K. Parker has pointed out to me) in the *Nautilus striato-punctatus* of Fichtel and Moll, which Mr. Parker considers to be the *Geoponus stella-borealis* of Ehrenberg, but to be really a Nonionine form of *Polystomella*. See Ann. of Nat. Hist. ser. 3. vol. v. p. 108.

in a radial direction (Plate XVII. fig. 2, *d*, *d'*, Plate XVIII. fig. 1, *f*, *f*), from the meridional canals of each convolution to the stolons which unite the segments of that convolution. These, which may be distinguished as the converging branches, are, however, much less regular in their distribution than those which pass outwards from the meridional canals to the stolons of the succeeding whorl.

191. Thus, then, it becomes apparent that by means of the two *spiral canals*, the number of convolutions of which equals that of the whorls of the shell,—the very numerous *meridional canals*, of which there is one for every segment of each whorl,—the vast multiplication of pairs of *diverging branches*, of which each meridional canal sends off a number equal to that of the connecting stolons between the segments,—and the very considerable aggregation of *converging branches*, which probably do not fall far short of the preceding except in being single whilst they are in pairs,—a very complete system of intercommunications is maintained between the external surface and even the innermost portions of the shell. That these passages are occupied, in the living animal, by prolongations of the sarcode-body, there can scarcely, I think, be any reasonable doubt; and when we look to the remarkable development of what has been elsewhere termed the "intermediate skeleton," but which may here be more appropriately termed the "supplemental skeleton,"—namely, the secondary calcareous deposit which not only forms the solid nucleus, but spreads itself over the entire surface, adding considerably to the thickness of the spiral lamina,—it cannot be deemed improbable that the special purpose of the canal-system is the formation and nutrition of this supplemental skeleton, which has obviously no direct relation to the segments of the animal body contained within the chambers. Through the trumpet-shaped diverging branches which open in such numbers upon the surface of those chambers, and the straight canals which arise from the nucleus, there will be abundant opportunity for the sarcode-body to extend itself over the whole exterior of the shell, and thus to form any additional deposit upon its surface.

192. Having carefully re-examined *P. crispa* with a view of ascertaining to what extent the canal-system is developed in it, I am enabled to state that I have found it to possess a canal-system distributed on the same plan with that of the organism we have been considering, but much more limited in its extent, as might be expected from the much inferior development of the "supplemental skeleton." In the vertical section represented in Plate XVII. fig. 9, we see the solid umbilical protuberances *a*, *a'*, traversed by straight canals, which terminate in the pits on their surface that were originally noticed by Professor WILLIAMSON, and supposed by him to give exit to pseudopodia. At *b*, *b*, *b'*, *b'*, we see the transverse sections of the spiral canals, from which the straight canals just mentioned may be presumed to proceed; and at *c c*, *c' c'*, we see plain indications of a system of interseptal canals, resembling those of *Operculina* in their aspect and distribution, but clearly homologous, in their relations to the spiral canals, with the meridional canals of *P. craticulata*. I have not been able to detect any indication that diverging branches are given off from them, to pass through the spiral lamina to the

external surface; and the absence of any such distribution accords with the absence in *P. crispa* of any of that supplemental calcareous deposit which so remarkably changes the aspect of the general surface in *P. craticulata*.

Genus Calcarina.

The type next to be described is one in which the supplemental skeleton and the canal-system both attain a more remarkable development than in any Foraminiferous organism that has yet fallen under my notice; and their mutual relation here becomes so obvious, that no reasonable doubt can be entertained in regard to it.

193. *History.*—The generic name by which this type is now known, and which indicates its resemblance in form to the rowel of a spur, was first conferred upon it by M. d'Orbigny in 1825; the organism itself, however, was previously well known, both in the recent and in the fossil state, having early attracted the attention of the collectors of minute Testacea through the singularity of its shape. It seems to have first received the name of *Nautilus Spengleri* from Gmelin, its specific designation having been conferred on it in compliment to Spengler, who was among the earliest to direct attention to it; and under this name it was described and well figured in several of its varieties in the 'Testacea Microscopica' of Fichtel and Moll (p. 84, plate 14. figs. *d–i*, plate 15. figs. *i–k*), who refer to the authors cited below* for previous notices of it. Spengler's specimens were from Amboyna and Coromandel; Schröter found the species in the Adriatic; Fichtel and Moll obtained their specimens from the Indian Ocean and from the Red Sea; and D'Orbigny received his from Madagascar, the Isle of France, Rawack, the Marianne group, Cayenne, and Martinique. The specimens on which my own descriptions will be founded were partly collected by Mr. Cuming in the Philippine Seas, and partly obtained by him from the Mediterranean, in the neighbourhood of Malta. This type may be said, therefore, to have a wide distribution through the seas of the warmer regions of the globe.

194. The fossil specimens of this type appear to have been first noticed in the cretaceous beds of Maestricht by Faujas†. They were described and figured by Lamarck‡ under the designation of *Siderolites calcitrapoides*; but he totally misunderstood the nature of the organism, which he grouped with the Corals, instead of among Polythalamia. The genus *Siderolina* has been adopted by M. d'Orbigny, who seems to have been entirely ignorant of the generic if not specific identity of the Maestricht fossils with his recent *Calcarina calcar*, as to which no doubt whatever is entertained either by myself or by Messrs. W. K. Parker and T. Rupert Jones§. It is stated by these observers (*loc. cit.*), that another variety of the same with shorter spines, occurring in

* Linnæus, Syst. Nat. xiii.; Gmelin, Syst. Nat. p. 3371, No. 10; Spengler, Schrift. dän. Gesellsch. Kopenh. vol. i. p. 373, pl. 2, fig. 9, *a*, *b*, *c*; Schröter, Einleit. Conch.-Kennt. vol. i. p. 756; Neue Literat. u. Beytr. z. Naturg. vol. i. p. 309, pl. 1, figs. 3–6; Schreibers, Conch.-Kennt. vol. i. p. 5, No. 10.

† Hist. Nat. de la Montagne de St. Pierre, à Maëstricht.

‡ Syst. des Anim. sans Vertèbres, 1801, p. 376; and Tableau Encycl. et Méthod. pl. 470, fig. 4, *a–k*.

§ Ann. of Nat. Hist. 3rd Series, vol. iii. p. 480.

the Eocene Tertiaries of France, has been described by D'ORBIGNY* under the name of *Rotalia armata*, and by DESHAYES† under that of *Calcarina rarispina*.

195. The following is the character of the genus *Calcarina* given by M. D'ORBIGNY in his 'Foraminifères Fossiles de Vienne' (p. 160). "*Coquille* libre, spirale, déprimée, très rugueuse, formée d'une *spire* enroulée sur le côté, entièrement apparente en dessus, embrassante en dessous, composée de loges prolongées en appendices marginaux, souvent très allongés, représentant, dans leur ensemble, comme la molette d'un éperon. *Ouverture* en fente longitudinale contre l'avant dernier tour de spire. Semblable aux *Rotalines* par son enroulement spiral, par ses deux côtés à peu près aussi convexes, par l'emplacement de son ouverture, ce genre s'en distingue par les très longs prolongements extérieurs de son pourtour, appendices singuliers qui font supposer, dans l'animal, un mode de sécrétion tout particulier." Of *Siderolina* he says (p. 116):—"*Coquille* libre, équilatérale, orbiculaire, encroûtée en dehors, composée d'une *spire* embrassante à tous les âges, ayant des appendices allongés au pourtour, interrompant, dans l'intérieur, la suite des loges. *Ouverture* contre le retour de la spire toujours masquée à la dernière loge. Les *Siderolina* se distinguent des *Nummulina* par les appendices du pourtour, qui, dans l'intérieur de la coquille, viennent interrompre la suite des loges obligées de passer de chaque côté." No mention is made of *Calcarina* in M. D'ORBIGNY's most recent summary of the classification of the Foraminifera (Cours Élémentaire de Paléontologie), this genus not being regarded by him as occurring in the fossil state; but he repeats his characterization of *Siderolinæ* as Nummulites the turns of whose spire are interrupted by testaceous appendages. It will presently appear that the conception which M. D'ORBIGNY has formed of the structure of this type is erroneous in so many particulars, that without the assistance of figures and models it could not be recognized by the generic characters which he has assigned either to *Calcarina* or to *Siderolina*.

196. A very correct general description of the structure of *Calcarina* has recently been given by Messrs. W. K. PARKER and T. R. JONES, in their valuable series of papers on the "Nomenclature of the Foraminifera‡"; but their information in regard to it having been almost entirely based on external characters, and their description being altogether deficient in those minuter details which it is my special purpose to record, a full account both of its internal structure and of the principal varieties of its external configuration will not be the less valuable to those who may have occasion to study this type.

197. *External Characters.*—The comparison of the form of this organism to that of the rowel of a spur sufficiently well characterizes the general aspect which it ordinarily presents, as shown in Plate XIX. figs. 1–4. The feature which most distinguishes it from other *Hélicostègue* Foraminifera (only some *Rotaliæ* and *Polystomellæ* presenting a slight approximation to it in this particular) is the presence of a set of rays or spines, variable alike in number, length, and direction, which diverge from the central disk.

* Ann. des Sci. Nat. tom. vii. p. 273, No. 22; and Modèles, No. 70.

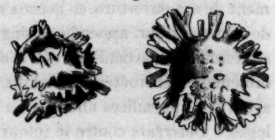
† Lyell's Manual of Geology, 5th ed. p. 228, fig. 236.

‡ Annals of Nat. Hist., Ser. 3. vol. v. p. 174.

These spines are usually few in young specimens, and become numerous with age; but this rule is by no means constant, since full-grown specimens are occasionally met with having no more than four or five very short spines (Fig. III. H). The spines are usually either cylindrical or somewhat club-shaped, the latter form being the more common; but we occasionally see them showing a tendency to bifurcation at their extremities; and they not unfrequently appear as if two, three, or even four spines had coalesced to form one,—this being indicated not only by its unusual size, but by the mutual divergence of its components as they extend themselves from the central disk (Fig. I. B, and Fig. II. F).

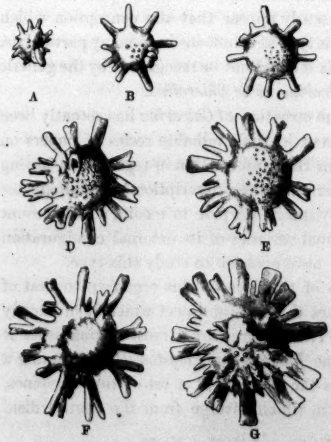
A somewhat remarkable contrast in the relative development of the disk and of the spines is presented by the general aggregate of the Philippine and Mediterranean specimens placed in my hands by Mr. CUMING; as is shown in comparing Figs. II. and III. It is in the former (Fig. II.) that we meet with the greatest number as well as the greatest relative length of the spines; and that the bifurcation or trifurcation of their extremities presents itself. In full-grown specimens of the Philippine *Calcarina*, we commonly find the spines diverging from the

Fig. I.



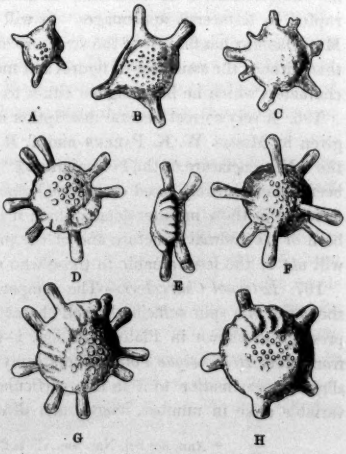
Two specimens of Philippine variety of *Calcarina*, distinguished by unusual exuberance of spinous outgrowths.

Fig. II.



Outline-representations of various specimens of Philippine variety of *Calcarina*.

Fig. III.



Outline-representations of various specimens of Maltese variety of *Calcarina*.

margin of the central disk in such abundance, that very little of that margin is left free. The length of their spines, moreover, at different ages, varies pretty constantly with the diameter of the disk, the average proportion being about two-thirds; though we occasionally meet with specimens in which the disk is unusually large and the length of the spines does not equal more than half its diameter, and others in which the disk is unusually small and the length of the spines is equal to its whole width. In the Mediterranean *Calcarinæ* (Fig. III.), on the other hand, I have seldom met with more than nine spines; and any excess beyond that number is only presented by specimens in which the disk is very large, so that wide intervals present themselves along its margin between the bases of the spines (Plate XIX. fig. 2). Their spines are nearly always simply clavate in form, any tendency to bifurcation or trifurcation at their extremities being rare; and they show but little disposition to increase in length with the enlargement of the central disk, being often not only relatively but even absolutely shorter in old specimens; as if the spines had entirely ceased to grow, and the disk had (as it were) included their basal portions within itself. In some instances, indeed, they scarcely show themselves enough to attract attention; being little more than tubercular projections from the margin of the disk (Fig. III. H). Notwithstanding, however, this strongly marked difference in general physiognomy, it becomes obvious, on the comparison of a sufficient number of individuals, that no line of specific distinction can be fairly drawn on such a basis between the Philippine and the Mediterranean forms; since among the Philippine we meet with not a few specimens, in which the spines are as few and simple as they are in the great bulk of the Mediterranean (Fig. III. B, C); and specimens not unfrequently present themselves among the Mediterranean (Plate XIX. fig. 2), in which there is not merely an addition to the ordinary number of the spines, but a manifest disposition in many of them to subdivide near their extremities, thus showing an obvious approximation to the Philippine type. Although the spines usually radiate nearly in the equatorial plane, yet it becomes obvious, when their connexion with the central disk is examined, that they originate at different levels (Fig. III. E, F); this will presently be found to depend on the fact that the form of the spire is not nautiloid but turbinoid. Besides the ordinary radiating spines, an extraordinary growth of short pointed spines is sometimes seen, either partially or completely covering one or both surfaces of the central disk (Fig. II. G); and examples occasionally present themselves (Fig. I. A), in which the development of these seems to have altogether superseded that of the ordinary radiating spines.

198. It is remarkable that among the very young specimens of this type, a yet greater variety shows itself than among those further advanced in life. In Plate XIX. figs. 5, 6, and 7, are shown what may be considered the ordinary or normal aspect of the very young *Calcarina*; whilst in figs. 8–11, and Plate XX. fig. 6, we have representations (under higher magnifying powers) of examples of what may be termed the *hispid* condition, which so frequently presents itself in small *Calcarinæ* as to give rise to a question whether they should not be made to constitute a distinct species. I have satisfied

myself, however, by the comparison of a large number of specimens, that so continuous a gradation presents itself between the smoothest and the most hispid specimens, as to render the attempt to separate them specifically altogether futile; and Mr. W. K. Parker, who has examined a yet larger number of specimens, fully confirms this conclusion. Moreover the internal structure of these hispid specimens, as shown in horizontal section (Plate XX. fig. 8), shows no departure whatever from the ordinary type.

199. Returning, now, to the external aspect of the fully-developed *Calcarina*, we have to notice that each surface of the disk is very commonly elevated, especially in its central portion, into rounded tubercles, more or less closely set together (Plate XIX. figs. 3, 4). These are sometimes large and prominent, and present the semitransparent appearance which is common among the like tubercles of *Operculina* (¶ 146); more commonly, however, they are less conspicuous either as to size, prominence, or distinctive aspect; and sometimes they are almost or altogether wanting (figs. 1, 2). Yet it is seldom, if ever, that they are absent from both surfaces of the disk; and it is more common to find them deficient on the surface nearest to the apex of the spire, than on that on which its last-formed chambers are visible. And even when no prominent tubercles are present, a distinction may be generally made out by careful examination in the parts of the surface corresponding to their usual situation. For whilst the exterior of the disk is marked, more or less conspicuously, with minute punctations (figs. 1, 3, 4), these are not to be seen on its tuberculated prominences; and the like deficiency is generally to be noted in circular spots of the surface, even when it is not raised into tubercles. Occasionally, though rarely, not even this mark of differentiation is seen, the punctations being uniformly distributed over the surface, which is in that case always the one nearest the apex of the spire.

200. The surface of the spines is marked, more or less conspicuously, by a longitudinal furrowing (figs. 1, 3, 4), not unlike that of the "marginal cord" of *Operculina* (¶ 156). The furrows maintain a general parallelism, but there are frequent inosculations between them; and punctations marking the orifices of deeper canals are often to be noticed at the bottom of the furrows.

201. One important feature of the external aspect of the disk has yet to be mentioned; namely, the indication of a *spire*, which more or less distinctly presents itself on one of its surfaces (Fig. II. B, Fig. III. D, G, H). This indication is sometimes limited to two or three chambers; but more commonly about half a turn may be distinguished, the spire becoming absorbed (as it were) into the solid mass of the disk, as we trace it backwards. The walls of the last-formed chambers, where entirely disengaged from the disk, are extremely thin (Plate XIX. fig. 4), so that it is rare to find them perfect; and an opening formed by the fracture of the wall of the newest chamber has been mistaken by MM. Fichtel and Moll, and apparently by M. d'Orbigny also, for the true aperture of the shell, which, as will presently appear, is of an entirely different character, and not easily to be distinguished. The prominent surface of the walls of the conspicuous chambers

of the newest whorl is covered with punctations resembling those of the general surface of the disk; but they are more minute and more closely set together, and they are distributed with great uniformity, no unpunctated spaces being anywhere visible.

202. *Internal Structure.*—When the internal structure of this organism is examined by means of thin sections taken in different directions, the apparent anomalies of its conformation are found to be dependent simply upon the extraordinary development of its "supplemental skeleton;" its general plan of structure being much simpler than the peculiarities of its aspect would seem to indicate. The spire, as laid open by vertical section (Plate XX. fig. 1), is turbinoid; consisting usually of about five whorls (a, a^1, a^2, a^3, a^4), that start as usual from a central cell, and progressively increase in size, each whorl being applied merely to the surface of the preceding, and not investing it in any degree, the chambers being altogether destitute of alar prolongations. The aspect of the spire as seen in equatorial section is shown in Plate XX. fig. 4; this section, being taken in such a plane as to cut through the outer whorls a^4, a^3, a^2, passes entirely over the surface of the two inner whorls a^1 and a. The disposition of the chambers, as indicated by such sections, is ideally shown in Plate XIX. fig. 12. The turns of the spire are separated from each other by the interposition of a thick layer of solid shell-substance; and this is quite distinct from the proper walls of the chambers, as may be well seen in Plate XX. fig. 4, where the walls of the newest chambers are shown at b to be entirely destitute of any such addition, whilst at b^1 in the preceding part of the same whorl we observe them encrusted by a thin additional layer d, and, as we trace this layer backwards to d^1 and d^2, we perceive that it progressively augments in thickness, until it acquires its maximum at d^2, just where it is covered by the subsequent whorl. This distinction between the proper walls of the chambers and the "supplemental skeleton" can be traced to the very centre of the spire. The septa are entirely formed by the infolding of the proper walls of the chambers, which are there flattened against each other so as to form two layers, which are usually in contact, but which sometimes diverge (especially near the external margin of the chambers) to give passage to canals. There does not appear, however, to be any regular "interseptal system" as in *Operculina* and *Polystomella*. The communication between the adjacent chambers of the same whorl is effected, as in *Polystomella*, through series of pores (fig. 1, c) disposed at pretty regular intervals along the inner margin of the septum*.

203. That the spines entirely originate from, and are strictly appendages of, the "supplemental skeleton" is well seen in fig. 4, which shows their connexion with its

* Messrs. Parker and Jones say (Ann. of Nat. Hist. Ser. 3. vol. v. p. 175) of the aperture of *Calcarina*, that "in well-preserved specimens of the typical forms, the real aperture, which is essentially a slit, as in the true *Rotaliæ*, becomes bridged over by delicate bars of shell-matter." I cannot but think that they have allowed themselves in this statement to be somewhat influenced by a foregone conclusion that "*Calcarina* is a subgenus of *Rotalia*." The examination of numerous sections of the character represented in fig. 5 leaves no doubt in my own mind that the aperture of *Calcarina* is essentially such as I have above described; and that if it occasionally in perfect specimens has the character of a continuous fissure (which I would by no means take upon myself to deny), such is an aberrant rather than the ordinary form.

successive convolutions. Thus the spine *e* is one of the oldest, being traceable inwards to the earlier whorls; whilst those marked e^1, e^2, e^3, e^4, e^5 are obviously of progressively later production, their respective origins being further and further removed from the centre of the spire. It is, moreover, to be observed that each spine receives an augmentation in thickness as the convolution from which it sprang is encircled by others; this augmentation, however, is not marked (as in the spines of *Echini*) by lines of demarcation between the earlier and the later formations; and there is every reason to believe that the growth of the spines, both in length and in diameter, is continuous rather than interrupted. Although it might seem, from the examination of such sections only as are taken in the direction of the equatorial plane or in one parallel to it, as if the course of the spire must be seriously interrupted by the radiation of the spines (which sometimes appear to be so interposed between consecutive chambers as completely to separate them); yet the fact is that owing to the turbinoid form of the spire, a spine projecting from an earlier whorl is very little in the way of even the next convolution; for as this passes by the spine on a different level, its chambers are but slightly encroached-on, and this only upon the side which looks towards the apex of the spire,—as will be readily understood by examining the relation of the last half-convolution, visible in such a specimen as the one delineated in Plate XIX. fig. 4, to the pre-formed spines, or by an inspection of the ideal represented in Plate XIX. fig. 12.

204. The canal-system of *Calcarina* presents a development so extraordinary in itself, and so obviously related to that of the "supplemental skeleton," as to throw great light upon its special functional destination. We do not here observe any such peculiar but limited distribution of systematically arranged passages, as that which constitutes so remarkable a feature in *Polystomella*; but every portion of the supplemental skeleton, with the exception of certain solid cones presently to be noticed, is traversed by canals which run very close together, with frequent inosculations, and which thus form a continuous network with long narrow meshes, that commences from the parietes of the chambers and extends itself to the very extremities of the spines (Plate XX. figs. 1, 2, 4). The proper walls of the chambers, as already stated, are uniformly perforated, like those of the chambers of *Rotaliæ*, by foramina of considerable size (averaging about $\frac{1}{3000}$th of an inch in diameter); with these the canals of the supplemental skeleton do not seem to be directly continuous, for they are of about double the diameter and lie further apart from one another; but immediately round the proper walls of the chambers (as shown in Plate XX. fig. 1) there seem to be irregular lacunar spaces, into which their foramina open externally, and from which the passages of the canal-system originate. How numerous and closely-set these passages are, is shown in Plate XX. fig. 3, which is taken (under a much higher magnifying power than the rest of the figures) from a section that passes through the supplemental skeleton just outside the walls of one of the chambers, in such a direction as to cut through the passages transversely or obliquely. These passages run in different directions; some proceeding directly towards the external margin of the convolution, and being

continued into the spines where these are given off from it; whilst others pass not less directly towards the two convex surfaces of the disk. In the earlier whorls of the spire, as shown in Plate XX. figs. 2 and 7, indications of spiral canals, commencing (as in *Polystomella*, ¶ 188) in a central lacunar system, are frequently traceable; and sometimes we may make out a general distribution of the canal-system of the earlier whorls (fig. 7) that strongly reminds us of that prevailing in *Polystomella* (¶ 189), the canals of the spines originating (as seen at *a*) in diverging branches which radiate outwards through the spaces left between the two layers of the septa. But this arrangement soon seems to be merged, as it were, in the much more copious distribution of passages that arise from the lacunæ round the proper walls of the chambers. The canals which pass towards the two surfaces of the disk soon lose the general uniformity of arrangement which they elsewhere present; for they become crowded together in some situations and separated in others, so as to leave a number of columnar spaces untraversed, whilst the intercolumnar spaces are copiously penetrated by them,—as is seen at *e*, *e*, *e*, in Plate XX. figs. 1 and 5, the one figure showing the solid columns divided longitudinally, and the other showing them as they are cut transversely. The varying appearances of the external surface, as described in ¶ 199, will now be understood. When, as commonly happens, the summits of the columns rise above the general level of the surface, they will show themselves as rounded tubercles. But when they are not thus elevated, they will merely be distinguished as circular spots surrounded by the punctations which are the orifices of the canals. In the spines, on the other hand, the canals form a longitudinally inosculating system (Plate XX. fig. 2), of which the branches near the surface usually reach it so obliquely as to pass along it for some distance as open furrows (¶ 200), the punctations seen in which are the orifices of branches that strike the surface at a greater angle.

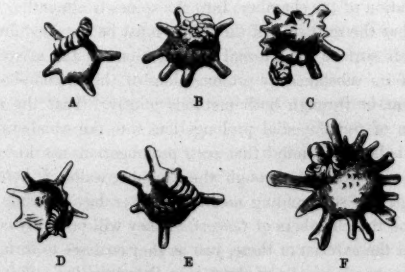
205. It is obvious from the foregoing description, that the statement of M. D'ORBIGNY as to the prolongation of the chambers into the spines is altogether erroneous; and it is further obvious that the nutrition of the spines must be provided for either through the investment of their surface by external prolongations of the sarcode-body, or through the penetration of its substance by prolongations of the sarcode-body conveyed into it by the canal-system, or through both methods jointly. That the sarcode-body is continued in the form of pseudopodial prolongations into the canal-system can scarcely be doubted, when it is borne in mind that such prolongations are known to pass through the pores which are scattered through the chamber-walls of *Rotalia*, and to extend themselves through the surrounding medium. After having made their way through the proper walls of the chambers of *Calcarina*, they will probably coalesce again in the lacunar cavities on the exterior of these, just as they coalesce to form a continuous layer of sarcode over the chamber-walls of *Rotaliæ* or *Polystomellæ*; and from the aggregation of sarcode in those cavities a new set of pseudopodial prolongations will take their departure through the canal-system of the "supplemental skeleton," just as a secondary set of pseudopodial filaments of sarcode are often seen to diverge from the little agglo-

merations formed by the reunion of some of those that primarily issue from the pores of the shell. The analogy of other Foraminifera, moreover, renders it very probable that the prolongations of the sarcode-body which reach the surface through the canal-system, will reunite upon it so as to form a continuous investment over the whole; and that this will be especially the case on the spines, appears to be indicated by the provision there is in the furrowing of the surface, for conveying the prolongations of the sarcode-body to every portion of their exterior.

206. Thus, then, by interpreting the structural phenomena presented by *Calcarina* according to the analogy of the facts which have been determined by observation of the living animals of the allied type *Rotalia*, we seem almost indubitably led to the conclusion that the canal-system is specially destined for the formation and maintenance of the "supplemental skeleton;" serving to convey prolongations of the sarcode-body from the segments which occupy the chambers, through the thick layer of solid shell-substance that is secondarily formed around those chambers, and through the prolongations of that layer which constitute the spines; and further, that it maintains a tolerably direct communication between even the innermost chambers of the spire and the external surface,—a connexion which would have been cut off by the interposition of the "supplemental skeleton," had not this been provided with some such system of intervening canals.

207. One more fact remains to be noticed, which is of much interest as showing that the growth of the spire and that of the "supplemental skeleton" are to a certain extent independent of each other:—I refer to the departure from the regular form that frequently shows itself in the later turns of the spire, which (so to speak) often "run

Fig. IV.



Abnormal specimens of *Calcarina*.

wild" in a variety of strange modes, examples of which are so well represented in Fig. IV. A–F, that it is unnecessary to refer to them in other than these general terms.

The extension of spines from the whole surface of the disk, in the mode represented in Fig. I. A, may in like manner be regarded as a sort of "running-wild" of the supplemental skeleton.

Genus TINOPORUS.

208. A more remarkable example could scarcely be adduced, of the necessity of a thorough examination of the internal structure of the skeletons of Foraminifera as a guide to the determination of their true affinities, and of the danger of relying upon external characters alone, than that presented by the type I am next to describe under the name *Tinoporus*; certain forms of which present so strong a superficial resemblance to many specimens of *Calcarina*, as to be unhesitatingly associated with them by every one who has not had his attention directed to the minute features of difference they present; whilst the plan on which it is constructed will be found to be essentially diverse.

209. *History*.—My reason for adopting this name is as follows. In the 'Conchyliogie Systématique' of DENYS DE MONTFORT (Paris, 1808), there is described and figured * under the name of *Tinoporus baculatus* a small polythalamous body, which he seems to have distinguished from the other varieties of *Nautilus* (*Calcarina*) *Spengleri* figured by MM. FICHTEL and MOLL, partly by the fewness of its spines, and partly by the difference of its structure as displayed in vertical section. And although his figure and description are alike inaccurate (the former, as has been pointed out by Messrs. W. K. PARKER and T. R. JONES†, being partly drawn from specimens of *Calcarina*), yet as I can scarcely doubt that he had before him a specimen of the type I am about to describe, I think it right to retain the distinctive designation he conferred upon it. The following is DE MONTFORT'S characterization of the genus:—"Coquille libre, univalve cloisonnée et cellulée, spirée et lenticulaire; têt granulé extérieurement; bouche semi-lunaire, placée vers la circonférence et sur un des côtés; dos caréné, armé de quatre pointes au plus; les deux centres bombés et relevés." Of the species *T. baculatus*, which served as his type of the genus, and of which he gives the fourth variety of the *Nautilus Spengleri* of FICHTEL and MOLL as a synonym, he says:—"Cette coquille, qui pour nous est la tête (type?) d'un genre nouveau et assez nombreux, ressembleroit à la nummulie ou camérine tuberculée et criblée, si elle n'étoit armée de trois pointes obtuses. Ces pointes sont intérieurement sillonées et tuberculées à la manière de quelques tubipores: la bouche de la coquille, placée sur un des côtés, est très remarquable, en ce qu'elle est petite et formée en demi-lune: la spire est cachée et intérieure. Les auteurs allemands que nous avons cités dans notre synonymie, y comptèrent au moins quatre-vingts cellules. Nous avons fendu cette coquille à demi par le milieu, afin de faire apercevoir la construction de l'intérieur, qui, cellulée sur divers plans, nous conduit naturellement aux nummulies, mais elle en diffère par ses bras ou pointes, qui sont constans, quoique leur

* Tome i. p. 147.

† Annals of Natural History, Series 3. vol. vi. p. 34.

intérieur présente une organisation qui n'est point cellulée mais tubulée. La couleur du tinopore baculé est blanche, flambée et teintée de jaune; la coquille est entièrement opaque. L'individu qui a servi de sujet à notre description venoit de la mer des Indes orientales; on le trouva dans le sable dont étoit remplie une coquille du genre casque; on rencontre encore les tinopores parmi d'autres coquilles microscopiques, sur les plages du golfe Arabique, ainsi que dans quelques éponges de la mer Adriatique. D'une pointe à l'autre, le tinopore que nous venons de décrire a deux lignes de diamètre." It is from the very distinct statement of De Montfort (borne out by the vertical section rudely represented in his figure) of the cellulation of the interior of this organism on different planes, so as to give to its vertical section somewhat the appearance of that of a Nummulite, that I am induced to believe that he had really distinguished *Tinoporus* from the type to which we now give the designation *Calcarina*. For, as we have seen, no such appearance is presented by vertical sections of *Calcarina*; whilst, as will presently appear, *Tinoporus* is made up of several layers of cells superimposed one upon another; and although its relation to *Nummulite* is really remote, yet the resemblance in aspect presented by vertical sections of the two may easily seem, to such as are unacquainted with the real meaning of their appearances, sufficiently close to justify the parallel.

210. I am not aware that any subsequent writer has adopted De Montfort's generic definition of *Tinoporus*, which seems to have been treated as one of his many valueless differentiations which systematists have agreed to disregard. In the 'Dictionnaire Universel d'Histoire Naturelle' it is noticed as a synonym of *Calcarina*.

211. The plan of structure presented by *Tinoporus* differs so remarkably from any that has been yet described, as well to deserve being fully detailed. But it presents an additional feature of great interest, in the light which it throws upon the structure and character of the remarkable fossil genus *Orbitoides*, which, though first named by M. d'Orbigny, was first described by me*, and is scarcely less important in its geological relations than *Nummulites* itself.

212. Before proceeding, however, to the description of *Tinoporus baculatus*, I shall give an account of the structure of a simpler form of the same type, by which that of *T. baculatus* will be better understood. The form to which I allude has a much wider geographical range; for though the largest and best developed specimens I have seen are those which I have obtained from Mr. Jukes's Australian dredgings, yet I have met with it also in collections from the Fiji Islands, Mazatlan, and the Canaries; and Messrs. Parker and Rupert Jones (by whom this type has been recently noticed under what I cannot but consider the inappropriate designation *Orbitolina*†) state that it occurs also in the East and West Indies, in the Mediterranean, and on the British coast as far north as Arran. To this type, which is destitute of the projections so remarkably characteristic of *T. baculatus*, the name of *T. lævis* may be appropriately given.

* On the Microscopic Structure of *Nummulina*, *Orbitolites*, and *Orbitoides*, in the Quarterly Journal of the Geological Society, February, 1850.

† Annals of Natural History, Series 3. vol. vi. pp. 32, 33.

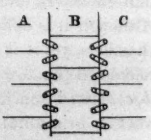
213. *External Characters.*—The largest examples I have seen of *Tinoporus lævis* present the form of a short truncated cone, much resembling the lower half of a sugar-loaf (Plate XXI. fig. 1, *a*), having its margins rounded off, and attaining at the base a diameter of about one-tenth of an inch. The base commonly exhibits a slight central depression (fig. 1, *b*). Sometimes the cone is more depressed, and spreads out more widely at the base; and in this case the basal concavity is usually wider and deeper. The examples I have seen from other localities have for the most part a spherical or spheroidal shape; but a careful examination will generally make it apparent that this shape is derived (so to speak) from that last mentioned, by the folding-inwards of its peripheral portion towards the centre of its lower surface, so as to leave a deep cavity at that part of the sphere,—the relation of the two forms being very much like that which exists between the expanded *pileus* of an Agaricus, and the same *pileus* whilst still included within its *volva*. I cannot regard these diversities of form as possessing any specific value; since they depend entirely upon mode of growth, and are not connected with any differences of internal structure.

214. In whatever form the *Tinoporus lævis* may present itself, it is recognized by the absence of projection or angularity, and by a regular areolation over its whole surface, which a good deal resembles that of the cuticles of many leaves, the areolæ preserving a tolerably constant average of size, but being very indefinite as regards form. The divisions are marked by very definite boundary lines; and in the interspaces between these, under a sufficient magnifying power, minute punctations may be seen.

215. *Internal Structure.*—When the structure of this organism is examined by means of sections taken in different directions, it is found to be composed of an aggregation of minute chambers of nearly uniform size, which are piled one upon another in pretty uniform layers, each of these presenting an approach to a concentric disposition (figs. 2, 3). Although it is difficult to make out with certainty the arrangement of the first-formed chambers, yet it is clear that as in other Foraminifera the point of departure is a spheroidal cell (fig. 3, *a*), which soon comes to be surrounded by a cluster of secondary cells (*b*, *c*) derived from it by gemmation. In what manner these are given off from the first,—whether by a spiral or by a cyclical extension of the sarcode-body,—I have not been able to satisfy myself, on account of the difficulty of precisely carrying the plane of section through this group of chambers. In *T. baculatus* I have been fortunate enough to do this in several instances, and have found that the early growth is unquestionably spiral (fig. 11),—soon, however, giving place to the cyclical, as in those varieties of *Orbitolites* whose growth commences after this fashion (¶ 54); and whether this be or be not the case in *T. lævis*, it is indubitable that before long the extension of the organism in diameter is effected by a budding-forth of new chambers from all parts of the circumference, not with such regularity, however, as to form distinct annuli as in *Orbitolites*. Whilst this extension is taking place peripherally, however, additional layers of chambers are formed, as in *Orbiculina*, above and below the central nucleus, meeting each other

on the equatorial plane; and in this manner the increase of the organism in thickness is effected. The growth on the two sides of the equatorial plane, however, is seldom or never symmetrical; and that of the more convex portion seems continually tending to overpower that of the opposite surface, so that the equatorial plane becomes more or less deeply concavo-convex. I have reason to believe that this inequality is due to the attachment of the flat or subconcave base to the surface of sea-weeds or zoophytes; in virtue of which it will naturally happen that the free side will grow faster than the other. It is by an excess of this predominating growth that the spheroidal form is acquired, with its deep residual cavity, as just now described.

216. On more minutely examining the structure of the walls of the chambers and the mode of communication between their cavities, we find ourselves carried back to the lower type of *Orbitolites* and *Orbiculina* in this particular,—that the septa are not double but single, and are formed of a simple homogeneous substance, presenting no vestige whatever of that fine tubulation which characterizes the dense almost ivory-like substance forming the walls of the chambers in the more elevated forms of this group. It will be convenient to speak of the partitions between the chambers as *horizontal*, when their general direction is parallel to that of the equatorial plane, and as *vertical* when that direction is perpendicular to it; their actual directions will of course vary with the curvature of the equatorial plane. The *horizontal* partitions or floors of the chambers are perforated by rounded apertures (Plate XXI. figs. 2, 3, 4) which closely resemble those of the shell of a *Rotalia* or a *Planorbulina* in their size and arrangement; and these will allow of free communication, by pseudopodial threads of sarcode, between the segments that are lodged in the chambers piled one over the other in a vertical direction. The *vertical* partitions are much thicker, and are not thus minutely and regularly perforated; but they exhibit a small and variable number of large apertures (fig. 4, *a*, *a*), that lead into the adjacent cells which lie in or near the same horizontal plane. I say *in* or *near*, because it is seldom if ever the case that the horizontal partitions or floors of two adjacent vertical piles of cells are on the same level; and, in fact, the typical arrangement (though frequently departed from) seems to be, that there is an *alternation* in the levels of the floors of adjacent piles (as shown in the accompanying diagram, based on some parts of fig. 3), and that every chamber in any pile B normally communicates with two chambers in each of its adjacent piles A and C, by one passage above and the other below the floor that divides them.



217. The relation of this interesting type of structure to that of *Planorbulina* appears to me so clear that it can scarcely be questioned. For, as in that genus, the first-formed portion of *Tinoporus lævis* will evidently consist of a flattened disk, consisting of numerous segments which are arranged in one plane, spirally in the centre of the disk, but clustered irregularly towards its circumference, and perforated on both sides with

numerous large pseudopodian foramina*. This relationship is admitted by Messrs. PARKER and RUPERT JONES; who state, however, that *Planorbulinæ* are differentiated by having "two or three tubular and margined apertures to each chamber, coarser pseudopodial pores, and no umbilical cells." Now I have shown that every chamber in the adult is connected with its adjacent chambers of the same or of alternate planes by two apertures; so that at the free growing margin of the young disk there would probably be at least two such pairs of apertures in the wall of every chamber. The difference in the size and number of pseudopodian pores is a very trivial character. And the superposed umbilical cells will probably be absent in the young *Tinoporus*, when as yet only a small number of rows of chambers have been formed around the central cell. I have, in fact, specimens in my possession which would be unhesitatingly characterized as *Planorbulinæ* by such as are unacquainted with the structure of the type we are considering; yet which I cannot help regarding as in all probability young forms of *Tinoporus*, having been found in the same dredging, and presenting just the characters which I should expect from analysis of the structure of the adult to find in them. Moreover, I have *Planorbulinæ* whose early growth is so distinctly spiral as to correspond in every essential particular with the young of *Rotalia*.

218. It is not a little remarkable, however, that this organism should also be very closely related to a body of which the true nature has hitherto been doubtful, viz. the *Millepora rubra* of LAMARCK†, the *Polytrema miniacea* of BLAINVILLE‡. This grows parasitically upon shells, sometimes spreading over their surface in a laminated form, sometimes rising into a sort of stem and sending off branches. I have ascertained by examination of thin sections, that it is composed of minute chambers piled together very much in the manner of those of *Tinoporus*, and having the same kind of communications; and as Mr. PARKER has in his possession a specimen of a nearly globular form, attached to a projection of a bivalve shell, it may be questioned whether the difference between the two organisms is even of specific value. For the mode of growth which ordinarily characterizes each, shows a tendency to pass into that of the other; *Tinoporus lævis* occasionally flattening itself out and extending marginally, whilst *Polytrema miniacea* occasionally restricts itself within a compact spheroidal form. The probable relationship of *Polytrema miniacea* to the Foraminiferous type has been already suggested by the sagacity of Dr. J. E. GRAY§; but as he was not acquainted with the internal structure either of *Tinoporus* or of *Polytrema*, he could not make a more particular approximation. I should add that the bodies described and figured by Professor MAX. SCHULTZE‖ under the generic name of *Acervulina* appear to me to belong to the same type. I have in my possession a specimen growing round the stem of a

* See Professor WILLIAMSON's Monograph of the Recent Foraminifera of Great Britain, p. 57.

† Hist. Nat. des Animaux sans Vertèbres, troisième edit., tom. ii. p. 309.

‡ Manuel d'Actinologie, p. 410, pl. 69. fig. 16.

§ Proceedings of the Zoological Society, April 27, 1858.

‖ Über den Organismus der Polythalamien, p. 67, plate 6. figs. 12–15.

zoophyte, like the *Acervulina acinosa* of SCHULTZE, but with more of the compactness of *Polytrema miniacea*.

219. I now return to the form of *Tinoporus* on which the genus was originally established, the *T. baculatus* of MONTFORT; which agrees closely with *T. lævis* in the fundamental characters of its organization, but differs in being furnished with a variable number of radiating appendages that give it a strong resemblance to *Calcarina*. Of the specimens in my possession, the greater part present the aspect represented in Plate XVIII. figs. 2, 3, 4, 5, and on a larger scale in fig. 6; and these were collected from coral reefs in various parts of the Polynesian Archipelago,—my earliest acquisition of them, however, having been from the contents of the stomach of an *Echinus* taken on the coast of Borneo, which were kindly put into my hands by Dr. J. E. GRAY. I am informed by Mr. DENIS MACDONALD that on certain coral islands which he has particularly examined, these organisms are so extraordinarily abundant, that they accumulate in the lagoons in regular strata, commonly alternating with strata of *Orbitolites*. The more massive and ruder forms represented in Plate XVIII. figs. 7, 8, 9, 10, occur in Mr. CUMING'S Philippine collection.

220. *External Characters.*—The typical form of the central portion of *T. baculatus* (Plate XVIII. figs. 2–6, and in section in Plate XXI. fig. 7) may be considered as an oblate spheroid; sometimes, however, it is nearly spherical, and sometimes it is much flattened out, especially when the body extends itself into the radial prolongations, as in Plate XVIII. fig. 4. Its surface is divided into areolæ (fig. 6) very much as in *T. lævis*; but the angles of junction of the partitions between the areolæ are very commonly occupied by rounded projecting tubercles, strongly resembling those of *Calcarina*. The number and size of these tubercles vary greatly among different individuals, as will be seen on comparing figs. 2 and 4, Plate XVIII*. From the marginal portion of the central disk there spring a variable number of conical prolongations having the furrowed surface of those of *Calcarina*; and these appear seated (so to speak) upon extensions of the central disk itself, which is sometimes so deeply subdivided at its margin as to resemble the body of a Star-fish (Plate XVIII. figs. 4 and 7), the areolar division being continued nearly to the extremity of each ray, and its point only being formed by the furrowed prolongation. These appendages are usually from 4 to 6 in number; I have occasionally seen only 2, and in no case have I met with more than 8. They usually diverge in or near the equatorial plane; but they sometimes come off in very different directions (Plate XVIII. figs. 8, 10).

221. *Internal Structure.*—The general organization of *T. baculatus*, brought into view by sections taken in different directions, does not differ in any essential respect from that of *T. lævis*; the origin of the whole aggregation of chambers in a central cell, their subsequent multiplication both horizontally and vertically, and their methods of communication in both directions, being all the same. As already mentioned, I have very

* They seem to be altogether wanting in the Philippine specimens, being apparently replaced by a multitude of small spines, which give to their surface a hispid aspect.

distinct evidence, in sections of this species, of a *spiral* commencement, soon giving place to an *irregularly-cyclical* growth; and sometimes the first-formed portion (Plate XXI. fig. 11, *a*) bears so close a resemblance to the innermost part of the spire of *Calcarina*, that in this earliest stage of their growth the two types could not be distinguished from each other. Thus *Tinoporus baculatus* seems to bear the same relation to *Calcarina*, that *T. lævis* does (through *Planorbulina*) to the *Rotaline* type (¶ 217). The essential difference between *T. baculatus* and *T. lævis* consists in the possession by the former of a "supplemental skeleton," which presents itself under two principal aspects. The piles of chambers extending vertically from the equatorial plane towards the two surfaces of the spheroid (Plate XXI. fig. 7) are partially separated by the interposition of pillars of solid shell (fig. 8, *a*); and it is by the projection of the summits of these pillars (as in *Calcarina*) that the tubercles of the surface are formed. The spines also, which form the extremities of the radiating prolongations, belong to the same system; and they are shown, by sections of the Philippine type that pass in a favourable direction (fig. 6), to be extended from a solid framework which begins to be formed even with the first convolution, and which adds greatly to the thickness of the partitions between the chambers, giving off a multitude of minute spines from their external surface (fig. 10, *c*, *c*). This framework is penetrated by a canal-system, which not only forms passages through the solid axis that is prolonged into the spines (fig. 10, *a*, *a*), but also extends itself into the partitions between the chambers (fig. 9, *b*, *b*). The canal-system of the solid axis, moreover, communicates freely with the cavities of the chambers that are adjacent to it, as shown at fig. 10, *b*, *b*. These chambers are arranged around it with considerable regularity, as is shown in fig. 5, which is a transverse section of the base of one of the radiating prolongations, showing the solid axis with its radiating canals, surrounded by three rows of chambers. It would seem as if, in the Polynesian variety of *T. baculatus*, the material of the supplemental skeleton were appropriated rather to the formation of the solid pillars than to that of a solid axis for the radiating prolongations; the latter being much less conspicuous than it is in the Philippine specimens, and sometimes appearing to be deficient altogether except at their extremities. On account of the variability of these differences, however, I cannot regard them as of any essential value.

222. If any further evidence had been required as to the essential relation between the "canal-system" and the "supplemental skeleton," I think that it must be satisfactorily furnished by the comparison of the two species of *Tinoporus* now described. For in *T. lævis* it is obvious that the system of communications which exists between its chambers is adequate for all the ordinary wants of an organism of this type, the structure of which is uniform throughout. But when, as in *T. baculatus*, an additional framework of solid walls is interposed in the midst of the building, for the support of the extensions into which it is prolonged, a special system of passages, originating from the cavities of the adjacent chambers, and extending throughout the solid framework, is provided for its nutrition.

223. With reference to the relationship between *Tinoporus* and the fossil genus *Orbitoides*, to which allusion has already been made, I shall here content myself with stating briefly that if the chambers of the equatorial plane of *T. lævis* were distinctly differentiated from those of the layers springing from it on either side, it would come to resemble in general conformation the simpler type of *Orbitoides* known as the *O. Mantelli*; and further that if, with this modification, there were also introduced the solid pillar-system of *T. baculatus*, we should have a corresponding resemblance to *O. dispansus**. The metamorphic condition of the shell of the fossil *Orbitoides* has hitherto prevented me from determining with certainty whether its elementary structure bears most resemblance to the inferior type presented by *Tinoporus*, or to the more elaborate structure of that of *Cycloclypeus*, to which type also it seems to be related†. On these points, however, I shall enlarge more fully elsewhere.

Genus Carpenteria.

224. Of all the Foraminifera collected by Mr. Cuming in the Eastern Seas, the last which I have to describe is perhaps the most interesting; since the type of structure which it presents is not only altogether new, but seem to furnish the connecting link (which had been previously rather suggested than supplied by *Thalassicolla* and its allies) between Sponges and Foraminifera,—two groups which accord most remarkably in their *grade of organization*, whilst they differ no less remarkably in *plan of structure*.

225. The larger number of the specimens of this type in the collection of Mr. Cuming are attached to the surface of a piece of *Porites* (coral); other specimens, however, are adherent to the shells of *Pecten* and *Cardita*; and the attention of Mr. W. K. Parker having been directed to these curious organisms, he has met with them on the surface of other bivalves, especially *Chama gigas*. It is not a little remarkable that the strong external resemblance which they present to the shells of certain sessile Cirripedes should have led not only Mr. Cuming, but other experienced conchologists, to regard them as belonging to that group. Their true nature was first suspected by Dr. J. E. Gray, who was led by his study of them to consider them as the testaceous envelopes of a Rhizopod intermediate between Sponges and Foraminifera; the grounds on which he came to this conclusion being, that he found the shell to be multilocular and minutely foraminated

* I should take this opportunity of stating that in my former description of *Orbitoides* (Journal of the Geological Society, Feb. 1850) I fell into the same mistake in regard to these pillars, that I did in regard to the analogous structure in Nummulites; regarding them as having been passages filled with solid calcareous matter in the process of fossilization,—an error which was pointed out to me by Professor Williamson at the time, and of which I have since come to be fully satisfied by the examination of the recent analogues.

† The figure given by Professor Ehrenberg, in his remarkable memoir already referred to, "Über den Grünsand und seine Erläuterung des organischen Lebens," plate iv. fig. 8, and by him designated as the internal cast of *Orbitoides javanicus*, will be seen on comparison to present a most remarkable correspondence with figs. 10, 11, 12 of Plate XXIX. (Phil. Trans. 1856) illustrating my description of *Cycloclypeus*.

like that of certain Foraminifera, whilst the fleshy substance occupying its chambers is strengthened with spicules like those of Sponges. Hence he considered this organism in the light of a *Sponge* enveloped in a shelly case with a single terminal *oscule*. My opinion as to its character having been asked by Dr. GRAY, I soon found reason to accord with him in his general idea of its affinities; the structure of the shell being most characteristically *foraminiferous*, whilst the substance occupying its chambers is no less characteristically *spongeous*. In communicating this result, however, to Dr. GRAY, I thought it right to suggest the possibility that this spongeous substance might be parasitic; the tendency of certain Sponges to find their way into even very minute fissures and passages having been observed by me in my researches on the structure of the Shells of Mollusks. Dr. GRAY agreed with me in thinking this improbable, for reasons which will be presently stated; and he communicated a general account of this new type (to which he did me the honour of giving my own name) to the Zoological Society*; at the same time expressing the desire that I should include a fuller account of its formation and structure in my communications on the Foraminifera to the Royal Society. With this desire I have now the satisfaction of complying.

226. *External Characters.*—The ordinary external aspect of *Carpenteria*, as represented in Plate XXII. figs. 1, 10 (taken from a group on the surface of *Porites*, of which the individuals are in close proximity to each other), at once suggests a resemblance to the Balaniform type; the shell being conical, attached by its broad base, furnished with a single definite aperture at its apex, and presenting an appearance of irregular divisions into triangular segments, which might easily be supposed to be "valves" bounding a single undivided cavity. On breaking into the interior of the shell, however, it immediately becomes apparent that the foregoing resemblance is superficial only; the entire cavity of the shell being divided into numerous chambers, which are completely separated from each other by septa, whose lines of junction with the external wall (indicative of the successional additions which the shell has received) give rise to the appearance of valvular divisions. And a closer examination reveals that these chambers are disposed upon a spiral type, each whorl completely investing (save on the adherent base) that which preceded it, so that only the external wall of the last whorl is anywhere seen on the surface. In the specimen represented in fig. 5, which is one of the isolated individuals occurring on the valve of a *Pecten*, the shell has a much less regular form, owing to the more or less complete divergence of the basal portions of the chambers of the last whorl, and the partial subdivision of some of those chambers into lobes which exhibit the like divergence. The shelly surface of the wall of each chamber presents a somewhat areolated aspect, which depends upon its being raised into a multitude of low rounded elevations (fig. 8); and under a sufficient magnifying power these areolæ are seen to be pretty uniformly marked with minute punctations (fig. 6). The form of the aperture at the summit of the cone, of which two examples are shown in figs. 13 & 14, presents a striking resemblance to that of the aperture of the *Milioloid* Foraminifera.

* Proceedings of the Zoological Society, April 27, 1858.

227. *Internal Structure.*—On breaking-away a portion of the external wall of the last-formed chamber, so as to lay open its interior (as shown in fig. 8), we find that its cavity is closed-in on every side by its shelly walls, except where it has communications (*b*, *c*) with the apical aperture; and each principal chamber is partially subdivided by a system of shelly septa, of which some are more and others less complete. The more complete of these secondary septa (fig. 8, e, e^1, e^2) resemble the principal septa (d, d^1, d^2) which separate the cavities of the chambers, in running from the base towards the apex of the cone; they divide the lower portion of each chamber into three, four, or more digitations, which are sometimes marked by an external lobulation, as shown in fig. 5; they stop short, however, about half or two-thirds of the way towards the apex, leaving the upper third or half of the chamber undivided. Some of these septa do not reach the opposite surface of the chamber; and the least complete (f, f^1, f^2) form a sort of network of ridges slightly projecting from the inner surface of the outer wall into its cavity (as shown in vertical section at *b*, *b*, *b*, fig. 15), and there marking out an areolation which corresponds to that of the external surface. The areolæ of the internal surface, however, are concave instead of convex; and the punctations, which are wanting on the ridges, are set more closely on the depressions between them. The reason of this peculiarity in their distribution will be presently seen (¶ 229).

228. The cavity of the last chamber communicates with the external orifice by a passage of considerable size; and the wall of this passage is distinctly continued as an irregular ring around the apical aperture, so that this aperture may be considered in one sense (as described by Dr. Gray) to belong to the last chamber alone. But it would be more correct to say that each cell as it is formed *conceals*, than (with Dr. Gray) that it *closes*, the aperture of the preceding cell; for a careful examination shows that the external aperture or vent is the termination of an irregular vertical canal, formed by the superposition of the oral rings of successive cells; and that through this canal the previously formed cells retain their original connexion with the exterior. In some of Mr. Parker's specimens, the oral ring is extended upwards into a tube or siphon at least equal in length to the radius of the cone. The general disposition of the chambers around the central canal is well shown by sections of the cone taken parallel to its base (fig. 7); such sections, however, may only bring into view the last or superficial whorl; and they will generally show only one or two chambers in communication with the vertical canal, the communicating passage of each chamber being on a different plane.

229. The foramina which pierce the outer wall of each chamber are of considerable size, as compared with the minute tubuli of *Cycloclypeus* and *Operculina* (see ¶¶ 103, 154), and they are not nearly so closely approximated; in both respects they correspond closely with the foramina of the ordinary *Rotaliæ* and *Globigerinæ*. In fig. 12 they are shown as they appear in a section traversing the wall somewhat obliquely to its surface, whilst in fig. 15 they are shown as they appear in vertical section; and in each case they are seen to present an annulated appearance, which is due to constrictions of the tubes at tolerably regular intervals. These tubes generally pass direct from one surface to the

other; but at *a*, *a*, fig. 15, it is seen that in the neighbourhood of the ridges which project from the inner wall into the cavity of the chamber, the tubes either bend or incline themselves in such a manner, that, whilst their *external* orifices are pretty uniformly distributed (fig. 6, *a*), their *internal* orifices do not show themselves upon the ridges, but are crowded together along their bases (fig. 6, *b*, and fig. 9). The septa, whether *primary* (separating the chambers from each other) or *secondary* (partially subdividing the chambers), are obviously formed by a doubling-in of the outer wall, so as to make each septum consist of two laminæ (fig. 12, *a*, *a*); this is seen also in sections of the incomplete septa (fig. 12, *b*), as well as of the ridges which may be considered as rudimentary septa (fig. 15, *b*, *b*, *b*). The two layers sometimes separate from each other, as shown in these figures, so as to leave intraseptal spaces; and these form a tolerably regular canal-system, which may be traced throughout the network of ridges that covers the inner wall of each principal chamber, and, through the primary septa, into the ring that surrounds the vertical canal (fig. 7, *g*, *g'*).

230. Whilst, therefore, the general plan of conformation of *Carpenteria* seems to differentiate it strongly from that of the ordinary Foraminifera, so close an alliance to them is indicated by the minute structure of its shell, that it becomes of special importance to determine whether its peculiarities are original, or whether they are acquired during the progress of development. I have fortunately been enabled to determine this point by the comparison of several specimens in different stages of evolution, and by the removal from the older specimens of one whorl after another until the original nucleus was arrived at (an operation which has been very dexterously performed for me by my draughtsman Mr. George West); and I can state without hesitation that the early condition of this apparently anomalous organism accords with that of the *Hélicostègue* Foraminifera generally,—its approximation being the closest to *Rotalia* in general form, but its tendency being rather towards *Globigerina* in this particular, that its chambers do not seem to communicate directly with each other, but that each has a separate external orifice directed towards the umbilicus. Various aspects of this first-formed portion of the shell, two of them showing the animal substance contained in the chambers, are seen in Plate XXII. figs. 2, 3, 4. Now supposing that a *Globigerina* were to grow in such a manner, attached by one of its surfaces, that the walls of its successively-formed chambers came into mutual contact, and that these chambers were so shaped and so piled one on the other as to give to the entire shell a conical form, each chamber opening by its own separate orifice into an umbilical funnel, we should have the essential type (so far as its shell is concerned) of *Carpenteria*; and this is really the mode in which the latter type is superinduced upon the former, as the development of the organism advances. It is further interesting to observe that the great size of the chambers which form the superficial whorl of *Carpenteria*, has every appearance of being due to the deficiency of that complete segmentation, in the later stages of growth, which characterizes the earlier; for every one of the *loculi* marked out by the ridges projecting into the interior corresponds so closely both in size and general aspect

with an entire chamber of the earlier whorl, that the areolation of the outer wall may be regarded as a sort of attempt at that complete subdivision of the cavity, which we have seen to be fully carried out in *Heterostegina* (¶ 114).

231. Thus, then, it appears that not only in the minute structure of its shell, but also in its general plan of conformation, *Carpenteria* essentially approximates to the ordinary Foraminiferous type, its affinity to the *Spongiada* being rather apparent than real; for although each cone does at first view seem to resemble the papilla of a Sponge enclosed in a shelly case with a terminal oscule, yet the internal structure of that cone does not bear out that resemblance. The link of affinity, however, seems to be supplied by the spongeous character of the animal substance which occupies the chambers (fig. 9); this (according to the evidence afforded by the dry specimens which alone I have had the opportunity of examining) not only possessing far more consistence than the sarcode-body of the Foraminifera, but being supported, in the large chambers at least (fig. 6), by sponge-like spicules (fig. 16), whose form resembles that of the simplest spicules of *Halichondria*, and whose composition is siliceous.

232. The idea which had occurred to myself of the possibly parasitic nature of this sponge-like substance, has been very strenuously advocated by Mr. Bowerbank, on the ground of the frequency with which the surface of dead coral and the valves of living as well as dead shells are covered with Sponges, and the consequent probability that any multilocular organism growing on such surfaces would be so penetrated by the sponge that all its chambers would be filled by the parasite. The following considerations, however, seem to me strongly to militate against such a view:—1st. That neither on the surface nor in the substance of the specimen of *Porites* covered with the cones of *Carpenteria*, nor on that of the valves of the *Pecten* and *Cardita* on which isolated specimens of *Carpenteria* occur, is there the least trace of spongy structure:—2nd. That, notwithstanding this marked difference in their *habitats*, all the specimens of *Carpenteria* yet examined have their cavities occupied by the same spongy substance:—3rd. That a firm brownish yellow substance of far greater consistence than the sarcode of Foraminifera, is found to occupy even the smallest and earliest chambers of *Carpenteria* (figs. 2, 4, *a*), filling them so completely that it can scarcely be supposed to be anything but the animal body properly belonging to them; and that although the substance in question is *there* destitute of spicules (the chambers being too small to accommodate them, as will be seen by the comparison of figs. 4 and 16, allowing for the difference of magnifying power), yet it is obviously the same with that in which spicules are copiously imbedded in the larger and later chambers:—and 4th. That notwithstanding the multitudes of sections of various Foraminiferous shells which I have made during the last ten or twelve years, I have never found their chambers to be occupied by a parasitic sponge of any description. I may add to these considerations the fact mentioned to me by Mr. Denis Macdonald, that he has met with various forms of branching Sponges*, possessing a peculiarly solid calcareous skeleton, and in many respects

* These specimens were collected during the voyage of H.M.S. 'Herald' in the Australian Seas, and

appearing to present the same kind of transition from Sponges towards Foraminifera, that, if my view be correct, is afforded by *Carpenteria* from Foraminifera towards Sponges.

233. The above reasons appear to me so strongly in favour of that idea of the essentially spongeous nature of the animal of *Carpenteria*, which had been from the first entertained by Dr. J. E. Gray, as to leave me little room for hesitation in the belief that such is its real character; so that, until the contrary shall be proved, we seem justified in regarding this curious organism as a Rhizopod which in virtue of its shell is *foraminiferous*, whilst in virtue of the animal body which that shell contains it is *spongeous*.

Concluding Summary.

[Added during the printing of the Paper.]

234. In bringing to a close the present series of Researches on the Organization of the Foraminifera, I think it desirable to combine a summary of the most important results which I have obtained, with some remarks on their bearing, not merely on the method to be followed in the attempt to frame a natural classification of this group, but upon some of those higher questions relating to the origin and value of differential characters generally, which have recently been brought prominently under the consideration of the scientific world. In so doing it is my desire to confine myself strictly to the scientific and practical aspect of these questions; seeking in the first place to determine, on the legitimate basis of induction, what general principles may be either certainly or probably educed from the comparison of the large body of facts which have been brought together by myself and others as regards the mutual relations of Foraminifera; and then briefly inquiring how far the results of similar comparisons made upon other types of organized structure justify the extension of the same principles to the Animal and Vegetable kingdoms at large.

235. It may be well for me to advert *in limine* to certain features in this inquiry, that render the group to which it relates singularly adapted for a comparison at once minute and comprehensive amongst a wide range of individual forms.—The size of the greater part of these organisms is so small, that many hundreds, thousands, or even tens of thousands of them may be contained in a pill-box; and yet it is usually not too minute to prevent the practised observer from distinguishing the most important peculiarities of each individual by a hand-magnifier alone, or from dealing with it separately by a very simple kind of manipulation. Hence the systematist can easily select and arrange in series such of his specimens as display sufficient mutual conformity, whilst he sets apart such as are transitional or osculant; and an extensive range of varieties may thus be displayed within so small a compass, that the most divergent and the connecting forms are all recognizable nearly in the same glance. I am not acquainted with any other

were transmitted by Mr. Macdonald to the Admiralty. I have not yet succeeded, however, in obtaining a sight of them.

group of natural objects, in which such ready comparison of great numbers of individuals can be made; and I am much mistaken if there be a single specimen of Plant or Animal, of which the range of variation has been studied by the collocation and comparison *under one survey* of so large a number of specimens as have passed under the review of Professor Williamson, Messrs. Parker and Rupert Jones, and myself, in our studies of the types to which we have respectively given our principal attention*.

236. The general fact which I desire to bring prominently forward as the result of recent investigations into this group, is, that in all the types possessing a wide geographical distribution, which have been specially studied by myself or by others, the range of variation has also been very wide; so that not only what would commonly be considered as *specific*, but such as have been regarded as *generic*, and in some cases even as *ordinal* differences, present themselves among organisms, which, from the intimacy of the relationship that is evinced by the gradational character of those differences as well as by the variations presented by the several parts of one and the same organism, must in all probability have had a common origin. And it appears to me to be a justifiable inference from this fact, that the wide range of forms which this group contains is more likely to have come into existence as a result of modifications successively occurring in the course of descent from a small number of original types, than by the vast number of originally distinct creations which on the ordinary hypothesis would be required to account for it†.

237. The greater part of my First Memoir was devoted to the investigation of the single type *Orbitolites*; and I there showed that not only as regards the size, shape, and other external characters of the organism as a whole, but even as regards the size and form of its elementary parts (in which greater constancy might be expected), is there so great a variation,—the most marked diversities being apparent even in different parts of the same individual,—that all attempts to found specific distinctions upon such variations are utterly futile. But further, I showed that a distinction on which almost any Naturalist would feel justified in relying as of at least *specific* if not of *generic* value,—that between the *simple* type in which the chambers are arranged on only one plane, and the *complex* type in which there are two superficial planes more or less strongly differentiated from the median,—is no less invalid. For although these types are usually distinguish-

* I have the authority of M. Deshayes for the belief, that the excessive multiplication of generic and specific distinctions which so greatly impairs the value of the late M. d'Orbigny's labours upon this group, was due to his having based these distinctions upon specimens selected for him as *typical*, and to his having disregarded the *transitional* forms which any large collection of these organisms is sure to exhibit in abundance,—thus, to use the admirably discriminating phrase of the late Prince of Canino, "describing *specimens* rather than *species*."

† In order to avoid misapprehension, I would here remark that the production of *any* organism seems to me just as much to require the exertion of Divine Power when it takes place in the ordinary course of generation, as it would do if that organism were to be called into existence *de novo*; the question being in reality, whether such exertion takes place in the way of continuous exercise according to a settled and comprehensive plan, or by a series of disconnected efforts.

able, the one from the other, without the least difficulty, yet they are often combined in the same individuals, and this in such a variety of modes, that the transition from the simple to the complex may be clearly seen, from the comparison of a sufficient number of specimens, to be by no means attributable to a mere advance of age. Further, having been furnished (by the kindness of Mr. H. J. Carter) with specimens of the Scindian fossil which presents the characters ascribed by M. d'Orbigny to his genus *Cyclolina*, I am now able most fully to confirm the suggestion I threw out on a former occasion (¶¶ 49, 70), that this genus is founded on a mere variety of *Orbitolites*, in which the character of the surface-marking is more than ordinarily cyclical.

238. Not merely, however, does the range of variation of this type confound the ordinary distinctions of systematists in regard to species and genera; it extends also to that difference in plan of growth, which has been assumed by M. d'Orbigny to be of such fundamental importance as justly to constitute the essential difference between his two orders *Cyclostègues* and *Hélicostègues*. For, as I have shown, although *Orbitolites* is typically cyclical from its commencement, yet specimens frequently present themselves in which its early development has taken place so completely on the helical plan, that if such had been collected before their assumption of the cyclical mode of growth, their essentially *Cyclostègue* character would not have been suspected.

239. Again, I have shown that a parallel variation is displayed by the genus *Orbiculina*, whose ordinarily helical plan of growth has caused M. d'Orbigny to range it among his *Hélicostègues*, notwithstanding that in fully-developed specimens its mode of growth is not unfrequently cyclical. The occasional exchange, in this type, of one plan of increase for the other, at an advanced period of life*, of which exchange I think I have given adequate evidence (¶¶ 85–87), is a fact which seems to me of very high interest, being much more decided in its nature than the corresponding change in *Orbitolites*. For whilst in the latter the tendency of the spiral form (whenever it presents itself) to pass into the cyclical, is apparent almost from the beginning, and the change is never long postponed, the helical plan is that on which the growth of the former not only commences, but continues to be carried on, often through the entire period of its increase.

240. It is important to remark that in each case the metamorphosis is simply due to the very rapid opening-out of the mouth of the spire, its two lateral extremities extending themselves round the shell on the one side and on the other, until they meet and completely enclose the portion previously formed (just as the lobes of the mantle in the adult *Cypræa* spread themselves round the shell until they meet on its dorsum); and also that the mutual relations of the chambers of the shell and of the segments of the animal body which they contain, remain essentially unchanged. Again, it is a point of no mean significance, that when an *Orbiculina* has undergone this change, the outer

* It has been remarked by Messrs. Parker and Rupert Jones, that whilst the assumption of the cyclical form in *Orbiculina* may often be the result of the continued growth of individuals under favourable circumstances, small starved forms also frequently take on the cyclical condition, leaving the young sublenticular stage without passing through the aduncal. See Annals of Natural History, March 1860, p. 181.

or cyclical portion of its disk can in no way be distinguished from that of *Orbitolites*; and that the only difference between these two types which has any semblance of validity, is the absence in *Orbitolites* of those successive encasings of the central nucleus, the presence of which seems to be a constant feature in *Orbiculina*. It is to be observed, however, that these successive encasings are due entirely to the extension of the later whorls of the spire over the earlier; and they are no longer formed in *Orbiculina* when the helical mode of growth gives place to the cyclical. Hence it seems not unfair to surmise that if the helical growth of an aberrant *Orbitolites* were to continue until its spire had made several turns, instead of stopping before the completion of one, its nucleus would receive successive investments from successive whorls, just as in the typical *Orbiculina*; and the only difference between these two types would thus vanish. On the other hand, if the helical growth of an *Orbiculina* were to give place to the cyclical at an unusually early period, the central nucleus would receive no investment, and would present the flatness by which that of *Orbitolites* is characterized when compared with that of the typical *Orbiculina*.

241. I cannot but believe that such as may have followed me through the details of my previous descriptions, will be disposed to agree with me in thinking it justifiable to assume that such a range of variation as to the *period* of the change in plan of growth, would be only analogous to that which both these types present in so many other particulars; and hence that the idea of the derivation of *Orbitolites* and *Orbiculina* from the same original is scarcely less probable than that of the derivation of the helical and cyclical types of *Orbiculina*, or of the simple and complex types of *Orbitolites*, from a common parentage;—particularly since, as was formerly pointed out (¶ 90), both types present analogous modifications in geological time.

242. Let us now apply the same mode of inquiry to *Alveolina*. It has been shown (¶¶ 93, 94) that this organism is closely allied in every other respect than its geometrical plan of growth to the types we have just been considering; the structure of the shell and its relations to the contained sarcode-body, and the relations of the segments of that body to each other and to the external world, being essentially the same in them all*. Now, however improbable it might seem at first sight, that an *Orbitolites* which extends itself as a flat or biconcave disk by successive concentric growths, and an *Alveolina* acquiring a fusiform shape by successive turns round a progressively elongating axis, should have had a common original, yet when the intermediate links are duly studied, a continuous gradation is found to be established. For, as has just been shown, a longer continuance of the helical mode of growth in which *Orbitolites* often commences, would really produce an *Orbiculina* with its centre so invested by successive

* I may take this opportunity of stating that the description which I based on the examination of sections of the shell has been fully confirmed by the internal casts obtained by Messrs. Parker and Rupert Jones from specimens whose chambers had been filled by an infiltration of silicate of iron (¶ 178); which casts most accurately represent the form of the sarcode-body and of its individual segments with their connecting stolons.

whorls as to form a vertical linear axis; and we find this axis in *Orbiculina* sometimes equalling in length the diameter of the spire, so that this organism at an early stage of its growth may be nearly spheroidal*. Now among the various types of fossil *Alveolinæ*, there are some whose shape, instead of being fusiform like that of the recent type I have described, is almost identical with that of a spheroidal *Orbiculina*; and the general structure of two such organisms will be so nearly identical, that I cannot see any difficulty in referring them to a common original. And when we examine a series of such fossil types, we see that they present a wider and wider divarication from the *Orbiculine* type in this one particular alone,—that whilst the later growth of *Orbiculina* tends to liken it to the discoidal *Orbitolites*, that of *Alveolina* tends to the continual elongation of its vertical axis, a difference which the analogies of the Foraminifera generally would indicate to be one of far foo small account to be fairly adopted as a ground of original distinction†.

243. In the assemblage of forms which I have thought myself justified in re-assembling under the designation *Peneroplis*, we encounter another remarkable series of variations, the principal of which have given occasion to the formation of the two additional genera *Dendritina* and *Spirolina*. With an exceedingly close conformity in the texture and in the superficial markings of their shells, as well as in their general plan of growth, we observe a marked diversity in the form and proportions of the spire, especially in the later stages of its growth, and a still greater divergence in the form and disposition of the septal apertures. For in the type to which M. D'ORBIGNY restricts the generic designation *Peneroplis*, we usually find the spire rapidly widening and becoming proportionally compressed in each succeeding convolution; whilst in that which he distinguished as *Dendritina*, the spire widens but slowly, whilst increasing rapidly in turgidity. Further, in the one type as in the other, the later extension is often in a straight line, instead of continuing to follow the spiral course; and on this variation alone, which is of no account whatever among Foraminifera (as will presently appear, ¶ 255), has been erected the genus *Spirolina*. Now in the typical *Peneroplis*, the septal plane presents a linear series of minute rounded pores; whilst in the typical *Dendritina* we find in their place a single large orifice with radiating extensions; the difference between these two modes of communication being as great as we find between almost any two types of Foraminifera whatever. Yet I believe that no one who will go through the details of the evidence I have collected from the study of transitional forms, will have any doubt that *Peneroplis* and *Dendritina* have had a common progenitor, and that the peculiarity in the mode of septal communication that characterizes each is intimately related to the compressed or turgid form of the spire in either case; whilst the different forms of the *Spirolina* type, among which we find the most remarkable

* See Philosophical Transactions, 1856, Plate XXVIII. fig. 8.

† In this view of the relation of *Alveolina* to *Orbiculina* I am supported by Messrs. PARKER and RUPERT JONES, who remark that *Alveolina* "may be said to represent a small thick *Orbiculina* drawn out transversely at its umbilici."—Ann. of Nat. Hist., March 1860, p. 182.

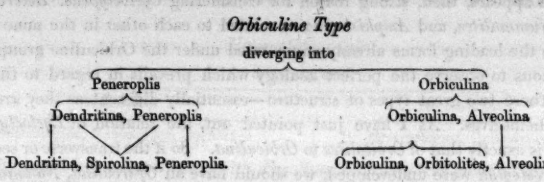
transitional conditions of aperture, are so obviously related to both the foregoing, that no reasonable doubt can exist as to their derivation from them. Now the geographical distribution of the two fundamental types is so far different, that where one prevails the other is either absent altogether, or presents itself under a modified form; and thus we seem justified in the belief that, whether either of them has been derived from the other, or both have been derived from some intermediate form (such as that which seems common alike to the *young* of both), the modifications which have given rise to the marked differences they now exhibit are mainly due to diversities in the external conditions under which they have been respectively propagated.

244. But to what other type does *Peneroplis* itself present the closest approximation? By systematists in general the intimate relationship which I have shown it to possess to the helical type of *Orbiculina* (¶ 130) has been so slightly regarded, that it has been considered as at least equally related to the *Operculine* type; and yet, as I shall presently show, these two types are removed from each other in all the most essential features of their structure, as far as any two polythalamous Foraminifera can be. And the idea of the derivation of *Peneroplis* from the same stock with *Orbiculina*, seems justified by the fact that the young forms of the two are frequently so alike as not to be distinguishable by external characters alone, whilst their internal difference consists only in the presence or absence of the secondary or transverse septa, a character which I have shown reason to regard as variable in this group* (¶ 130).

245. Notwithstanding, therefore, the apparently wide divergence of the cyclical *Orbitolites*, the helical *Orbiculina*, the fusiform *Alveolina*, and the simply-chambered *Peneroplis* and *Dendritina*, these several types must be regarded as most intimately related to one another; and that relationship seems to me much more likely to have arisen from a common ancestral descent, than from the original creation of independent types capable of graduating into each other so continuously as almost to assume each other's characters. It is very important to remark that they all possess that peculiar texture of shell, which is designated by Professor WILLIAMSON as *porcellanous*; presenting an opake white hue when seen by reflected light, but a rich brown or amber colour when seen by light transmitted through thin natural lamellæ or artificial sections. This substance is entirely structureless, and possesses no great density or tenacity. Moreover in all the foregoing types, each of the septa intervening between the chambers consists of only a single layer; the passages of communication between them are for the most part so large and free, that the segments of the sarcode-body are but very imperfectly isolated from each other; and, as might be anticipated from this incompleteness of separation, it is here that variations in the mode of communication between the chambers seem to be of

* My statement on this point is fully confirmed by Messrs. PARKER and RUPERT JONES; who state that "not unfrequently, feebly-developed peneropliform varieties, as well as good-sized adunciform specimens, occur, in which the long narrow chambers are at times simple and undivided, being occupied by transversely elongate lobes of sarcode, instead of numerous minute subcubical blocks." See Ann. of Nat. Hist., March 1860, p. 180.

least account. It is in this type that we recognize the nearest approximation towards such forms as *Thalassicolla*, which seem to connect *Orbitolites* with *Sponges* (¶ 67); while the relationship which *Orbiculina* and *Peneroplis* have been supposed to bear to the ordinary *Hélicostègues*, being dependent only on plan of growth, and being utterly at variance with the essential characters of the two groups, must be regarded as one of analogy, not of affinity. Looking to the evidence already adduced in regard to the prevalence of particular modifications of *Orbitolites* in particular localities (¶ 62), and to the influence of the geographical distribution of the *Peneroplis* type upon the modifications it presents (¶ 138), we seem justified in extending the same view to those larger (though not more essential) differentiations which these types must have undergone on the hypothesis of their derivation from the same original. The following may be suggested as the mode in which the existing forms might thus have diverged from each other and from their primary type.



246. Passing on, now, to an essentially different group, that which includes *Nummulites* and its allied forms, we find that the relation of the discoidal *Cycloclypeus* and the helicine *Heterostegina* is of essentially the same nature with that of *Orbitolites* and *Orbiculina* (¶¶ 113, 116); the minute structure of the shell and the physiological condition of the sarcode-body being essentially the same in the two organisms, and the only important divergence between them being in their plan of growth. From the rarity of *Cycloclypeus*, all the known specimens of which have been brought from one locality, I have not yet had the opportunity of ascertaining whether it ever presents in an early stage any approximation to the helical mode of growth; but such a deficiency of affirmative evidence is obviously not equivalent to a disproof of what has strong analogy in its favour.—The variations which I have described among the different forms of *Operculina*, although limited to the form of the spire and the character of the surface-markings, would be amply sufficient to justify the erection of numerous species, were it not for the connexion established between the most divergent forms by intermediate links, and the necessity for an almost indefinite multiplication of hypothetical originals which the adoption of such a method would involve. The existence of such a large extent of variation among the specimens collected in the same locality must be admitted as valid evidence of the facility with which differential characters develope themselves in this type; and a strong probability is thus afforded in favour of the varietal character of larger differences among individuals whose conditions of existence are very diverse.

Hence the analogy of *Operculina* affords good ground to surmise that many of the reputed species in the nearly-allied genus *Nummulites* have no real title to that rank; the differences among many of them being not nearly so great as those we have met with among the varieties of *Operculina*; whilst those presented by many others do not exceed what might be reasonably expected to occur under a greater variety of modifying agencies. But I have shown (¶ 162) that it may be fairly questioned whether there is adequate ground for upholding the generic distinctness of *Operculina* and *Nummulites*; the characteristic by which the latter has been asserted to be specially distinguished being not unfrequently observable as a varietal difference in the former. The form which I have described under the designation of *Amphistegina Cumingii** bears a striking resemblance to the ordinary Nummuline type in the early part of its growth, and to the ordinary Operculine in the later; and may be regarded as in many respects a connecting link between the two.

247. There appears, then, strong reason for considering *Cycloclypeus*, *Heterostegina*, *Operculina*, *Nummulites*, and *Amphistegina* as related to each other in the same manner and degree as the leading forms already enumerated under the Orbiculine group. And it is very curious to observe the perfect analogy which prevails in regard to the forms under which these two great types of structure—essentially different as they are—tend to develope themselves. As I have just pointed out, the relation of *Cycloclypeus* to *Heterostegina* is exactly that of *Orbitolites* to *Orbiculina*. So if the transverse or secondary septa of *Heterostegina* were undeveloped, we should have an *Operculina*, *Nummulina*, or *Amphistegina* (these three types being in my view essentially one and the same), just as the like deficiency actually occurring in *Orbiculina* gives to it all the essential characters of *Peneroplis*. And the parallelism seems to be completed by the existence in *Fusulina*† of the same elongated condition of this type, that *Alveolina* is of the Orbiculine.

248. The mutual accordance of all these in the highly elaborated texture of the shell, in the relation which this bears to the segments of the sarcode-body, and in the presence of an intermediate skeleton with its canal-system, is extremely close. The substance of the shell is very dense, and of almost vitreous transparence where it is not perforated by the minute closely-set tubuli which usually pass direct from the interior of the chambers towards the external surface. Each segment of the body has its own proper envelope, so that the septa between the chambers are composed of two distinct laminæ, which diverge from each other where they give passage to the canal-system, and which are often further separated by the intervention of a portion of the "intermediate skeleton." The passages of communication between the chambers are so narrow, that the segments

* It is questioned by Messrs. Parker and Rupert Jones whether this is a true *Amphistegina*, chiefly on account of its bilateral symmetry (Ann. of Nat. Hist. Feb. 1860, p. 111). But I have met with perfect bilateral symmetry in specimens warranted as *Amphisteginæ* by those excellent judges of that type.

† I have not yet been able to satisfy myself as to the precise affinities of *Fusulina*, the metamorphic condition of its shell interfering with the minute study of its structure; but my view of its nature essentially corresponds with that of Messrs. Parker and Rupert Jones. (See Quart. Journ. of Geol. Soc., Nov. 1860, p. 458.)

of the body are much more isolated from each other than they are in the type already described; and the proper walls of the chambers seem, as it were, to be moulded upon the segments, instead of merely filling up the interspaces between them. This filling-up, in fact, is the office of the "intermediate skeleton," which gives a solidity to the whole aggregation that would otherwise be wanting; and special provision, as we have seen, is made in the canal-system for its nutrition. Altogether this type is the one in which the Foraminiferous structure attains its highest development, and which is most completely differentiated from every other. And the morphological variations it is known to undergo seem to me fully to justify the inference, that such further variations as have been shown to occur in the Orbiculine type might be regarded as the probabl source of the divergence, from some common ancestral stock, of the several forms whose intimate relationship I have demonstrated. The analogy of that type would suggest *Heterostegina* as presenting the nearest existing approximation to such a common original; and the stages of differentiation may be thus expressed:—

Heterostegine type
diverging into
Operculina — Amphistegina, Nummulites, Operculina.
Heterostegina — Heterostegina, Cycloclypeus.

From my imperfect acquaintance with *Fusulina*, I do not feel justified in expressing its exact relationship to either of the forms included in this scheme; and for the same reason I abstain from connecting *Orbitoides* with *Cycloclypeus*, to which it has some features of close relationship.

249. After this detailed examination of the general relations of the principal modifications of two of the most strongly marked types to be found in the whole group of Foraminifera, it seems needless for me to do more with respect to the other forms whose structure I have investigated, than to inquire how far the peculiar characters by which they are respectively distinguished show evidence of a like variability.—Thus we have seen that *Calcarina* is essentially distinguished from *Rotalia* by the extraordinary development of the "supplemental skeleton," and by the extension of this into radiating prolongations. But it has been shown (¶ 197) that the number, form, and proportions of these prolongations are subject to very considerable variations; so that whilst they are sometimes so greatly multiplied and prolonged as to constitute the principal feature of the organism, they are so little developed in other instances that the contour of the disk is scarcely interrupted by them. Further, it has been shown (¶ 207) that the development of this supplemental skeleton is in great degree independent of that of the spire; hence if this last be the essential component of the organism (as all analogy indicates), the supplemental skeleton must be regarded as a feature of minor importance. On the other hand, the development of radiating outgrowths is an occurrence not unfrequent among other helicine Foraminifera, even in species whose typical form is altogether

destitute of them (as Professor WILLIAMSON has pointed out in *Polystomella crispa*); and such forms differ much less widely, as regards this character, from the simpler forms of *Calcarina*, than these last do from the very complex forms which have been shown (¶ 197) to be connected with them by a continuously gradational series. Hence I cannot regard the remarkable development of the supplemental skeleton in *Calcarina* as affording any disproof of the idea of its genetic relationship to *Rotalia*, to which its affinity in every other particular is most intimate.

250. If, again, we inquire into the import of that remarkable development of the *canal-system*, which seems to be the distinctive feature of *Polystomella*, we find that if we base our judgment upon a sufficiently wide foundation of facts, its non-essential character becomes apparent. For although the large *P. craticulata* of the tropical and Australian seas presents the most symmetrical and extensive distribution of the canal-system that I have anywhere met with (¶¶ 187–191), the little *P. crispa* of our own seas exhibits but feeble traces of it (¶ 192); yet of the intimacy of their relationship no doubt can be fairly entertained. We have traced a parallel difference between the gigantic *Amphistegina Cumingii* and the comparatively diminutive *A. gibbosa* (¶ 171). And the like difference has been shown to exist between the two forms of *Tinoporus* (¶ 222), where its presence or absence is obviously associated with the presence or absence of the radiating prolongations and of the supplemental skeleton from which these proceed.

251. In considering the import of the canal-system as a character for the systematist, the mode of its formation must not be left out of view. I have shown that the passages which altogether go to make up this system are not true *vessels*, but are mere *sinuses*, left in some cases by the incomplete adhesion of the two contiguous walls which separate the adjacent chambers, and in other cases apparently originating in the incomplete calcification of the sarcode which forms the basis of the solid skeleton; certain portions of that substance remaining in its original condition, so as to maintain a communication between the contents of the chambers and the parts of the calcareous skeleton most removed from them, analogous to that which the Haversian canals afford in the case of laminæ of bone not in the immediate vicinity of a vascular surface. As, therefore, the development of the Haversian system is related to the thickness of the bone-substance to be nourished, so does that of the canal-system in Foraminifera seem to be related to that of the consolidating substance which constitutes the supplemental skeleton. And it is to be specially observed that nearly all the forms in which (so far as we know at present) it attains any considerable development, are denizens either of tropical or of sub-tropical regions, in which the influence of external conditions appears specially to favour the largest growth and the most specialized evolution of the Foraminiferous type.

252. I think it better, in the present limited state of our knowledge of two of the types to the elucidation of whose structure the present memoir has been devoted, viz. *Tinoporus* and *Carpenteria*,—to forbear to speculate further than I have already done upon their relationship to the forms already familiar to systematists (¶¶ 217, 230).

And I have now to show that the results of my inquiries in regard to such typical forms of Foraminifera as have passed under my review, are in complete accordance with those obtained by other naturalists who have proceeded upon the like method,—that of the comparison, not of selected specimens, but of entire gatherings over extended areas and through various geological epochs.

253. Long ago did those excellent observers MM. Fichtel and Moll (1803) manifest a clear perception of the wide range of variation to which certain types of Foraminifera are liable, and give admirable descriptions and figures of such varieties. But their views were too philosophical for the species-making systematists of their time: thus we find Montagu remarking of the forms which they ranked under the designation of *Nautilus* (now *Cristellaria*) *calcar*, "If these can be admitted as the same species, we may bid adieu to specific definition;" whilst out of the same series Denys de Montfort constructed no fewer than nine genera. It has been most unfortunate for the advance of this inquiry, that M. d'Orbigny should have prosecuted it under the influence of those ideas in regard to the differentiation of specific types, which he brought to the study of Foraminifera from that of the testaceous Mollusks to which he originally regarded them as allied; and that the influence of his comprehensive labours and high reputation should have given to his views, alike on the detailed arrangement and on the general classification of this group, a currency to which their entire inconsistency with its natural affinities entirely negatives their claim.—It was in studying one of the simplest types of this series, that Professor W. C. Williamson was led (1847) to perceive "the extraordinary capacity for variation which *Lagenæ* exhibit in different states and ages; extreme forms which appear to be very distinct from one another being connected together by specimens of an intermediate aspect to an extent only to be believed by those who examine a large series of specimens side by side*." And he adduced strong evidence, not only that most if not all of its reputed species are only varieties, but that the difference which separates the genus *Lagena* from *Entosolenia*,—viz. that the neck of the flask-shaped body is prolonged inwards in the latter, instead of outwards as in the former,—may be merely varietal. A like conclusion, strengthened by the results of his and my researches in regard to other types, Professor Williamson has extended to Foraminifera generally, in his beautiful Monograph of the Recent Foraminifera of Great Britain (1857). "It may now be regarded," he says, "as an established truth, that most of the external characters on which both earlier and later writers relied for distinguishing their species, possess but little value. The direction of growth in these shells, and the sculpturing of their exteriors, are alike influenced by age and local circumstances; hence a dissimilarity between the different stages in the development of the same individual, such as finds few parallels amongst the Mollusca with which Conchologists have so long identified them." Again, he remarks, "Nothing is easier than to throw the Foraminifera obtained by dredging over some limited area into defined groups, each of which has apparently a specific value. But as we extend our researches to more distant localities, new and intermediate forms perplex our minds as to what are the same

* Annals of Natural History, Jan. 1848, p. 10.

and what different species. Long before our dredging-net has swept round the British coasts, we find that what was already difficult trenches on the impossible; and when we test our results by applying them to collections made in remote parts of the globe, we become convinced that the limited amount of our information makes that impossibility absolute. *The more extensive our experience, the weaker become our convictions respecting the limits of variation in any species**."

254. The relations of the forms belonging to the family *Miliolitidæ* have recently been investigated by Mr. W. K. Parker† on the same method of extensive and minute comparison; and his results are not only in perfect harmony with those obtained by Professor Williamson and myself, but even go beyond them in generality. Thus in each of the genera *Cornuspira*, *Hauerina*, and *Vertebralina*, Mr. Parker reduces all the reputed species to one, while he shows that even their generic differences are really but of small account. And he not only in like manner reduces all the reputed species of the genus *Miliola* to the level of varieties, but brings down to the same rank the reputed genera *Spiroloculina*, *Biloculina*, *Triloculina*, and *Quinqueloculina*; the differences between which, arising from asymmetrical growth, and from variations in the form and number of the chambers, cannot be regarded as even of specific value, the Milioline plan of construction being preserved throughout. "If," he remarks, "the forms kept themselves as distinct as those represented in the diagrams, a naturalist might be excused for regarding them as distinct types; but between any two of these there may readily be found innumerable gradations, in large and small specimens, in the smooth and ornamented, in the shelly or the sanded, in attenuated and in distended individuals, and in specimens with symmetrical or non-symmetrical, or with two- or three-sided shells." I may add that I am fully prepared to endorse these conclusions; since they are entirely borne out by my own experience as to such forms of the Milioline type as have fallen under my notice.

255. In the large group of *Nodosarinæ* which has been carefully studied by Messrs. T. Rupert Jones and W. K. Parker, those gentlemen have felt themselves justified on the like grounds in reducing a multitude of reputed genera and species to a single type. Between the nautiloid *Cristellariæ* and the straight moniliform or rod-like *Nodosariæ*, which agree in essential characters of structure and mode of growth, they find such a continuous series of connecting links, that no line of demarcation can be anywhere drawn,—the straight, the curved, and the spiral forms passing gradationally one towards another. And the extreme forms being thus brought together, the various intermediate grades which have been distinguished by systematists under the generic names of *Glandulina*, *Lingulina*, *Dentalina*, *Rimulina*, *Vaginulina*, *Planularia*, *Marginulina*, *Dimorphina*, *Flabellina*, and *Frondicularia*, necessarily fall into the same category‡.

* Introd. pp. ix, x. † Transactions of the Microscopical Society, 1858 (New Series, vol. vi.), p. 53.

‡ Annals of Natural History, Nov. 1859, p. 477; and Quarterly Journal of the Geological Society, Aug. 1860, p. 302, and Nov. 1860, p. 454.

256. The same general doctrine having thus been shown to hold good in regard to all the chief natural subdivisions of the Foraminiferous group, it is not my purpose at present to prolong the inquiry in this direction. The systematic study of this tribe needs to be prosecuted far more extensively than my own time and opportunities have admitted, to enable even an outline-scheme to be framed, which should represent an approximation to the true relations of its principal families. But I think I have made it clear that such a scheme will be most likely to approach the truth, when the basis of it is laid in a thorough knowledge of the nature and extent of those variations which every chief modification of this type shows itself so peculiarly disposed to exhibit, and when, in building it up, the idea of *natural affinity* is accepted as expressing not only degree of mutual conformity, but *actual relationship arising from community of descent* more or less remote. For the occurrence of endless gradational departures from any types which we may assume as fixed, and of links of connexion between such as present the best-marked differentiations, seem to me to point unmistakeably to this as the only means of escape from that difficulty of indefinite multiplication which attends the doctrine of distinct specific creations when applied to a group in which scarcely any two individuals are alike. The case, in fact, is very analogous to that of the relationship between the various members of the family of Mankind; for whilst the historical evidence of actual change in them is so incomplete as well as so limited in its range, as to be quite inadequate of itself to establish their community of descent, yet when that evidence is considered in its relations to analogous facts drawn from the far greater variations of domesticated animals, and to the manifold gradations by which the extreme types are connected, physiologists of the highest eminence have felt themselves justified in accepting that community as probable. Now the modifications which any single type of Foraminifera must have undergone, to give origin to the whole series of diversified forms presented by that group, are not greater in comparison with those of which we have direct evidence, than are those which the advocate for the Specific Unity of the Human Races has no hesitation in assuming as the probable account of their present divergence.

257. This view of the case derives great force from the fact, that there is strong reason to regard a large proportion of the existing Foraminifera as the direct lineal descendants of those of very ancient geological periods;—a doctrine first advanced by Professor Ehrenberg in regard to a considerable number of Cretaceous forms; since fully confirmed and extended as regards the Tertiary fauna by the admirable researches of Messrs. Rupert Jones and Parker on the Rhizopodal Fauna of the Mediterranean, as well as by my own comparison of the recent and fossil types of *Orbitolites*, *Orbiculina*, *Alveolina*, *Operculina*, and *Calcarina*; and shown to be applicable also to the Secondary fauna, as far back as the upper part of the Triassic system, by the remarkable results of the investigations of the same gentlemen in regard to a well-preserved sample of it. Following out, by laborious and extended comparison, the method of inquiry I have so much insisted on, they have found ample evidence that the fact of a wide range of varia-

tion in this group is not confined to the present epoch, but that it is true also of the Foraminiferous fauna of all the geological periods to which their researches have extended. "Our own experience of the wide limits within which any specific group of the Foraminifera multiply their varietal forms, related by some peculiar conditions of growth and ornamentation, has led us to concur fully with those who regard nearly every species of Foraminifera as capable of adapting itself, with endless modifications of form and structure, to very different habitats—in brackish and in salt water,—in the several zones of shallow and abyssal seas,—and under every climate, from the Poles to the Equator. In arranging our synoptical tables of the Mediterranean Rhizopoda, recent and fossil, and in comparing their numerous specific and varietal forms one with another, we have not confined ourselves to our collections from this region, but have necessarily made comparisons of forms from almost every part of the globe, from the Arctic and the Tropic Seas, from the temperate zones of both hemispheres, and from shallow as well as deep-sea beds. Geologically, also, we have reviewed the Foraminifera in their manifold aspects, as presented by the ancient Faunas of the Tertiary, Cretaceous, Oolitic, Liassic, Triassic, Permian, and Carboniferous times; finding, to our astonishment, that scarcely any of the species of the Foraminifera met with in the Secondary rocks have become extinct; all, indeed, that we have yet seen have their counterparts in the recent Mediterranean deposits. This is still more clearly found to be the case with regard to the Chalk of Maestricht and the Tertiaries*."

258. The same excellent observers, in summing up their description of the Foraminifera of the blue clay met with in the alabaster pits at Chellaston near Derby, belonging to the Upper Triassic series, thus express themselves:—"Having thus pointed out that, judging from these specimens obtained at Chellaston, the minute *Nodosarinæ* and other Foraminifera of the Triassic period have continued to exist through the intermediate ages to the present day without losing any of their essentially specific features, we will observe that the *Nodosariæ* are present in rocks of still greater age than the Trias,—namely, the Permian and Carboniferous, and probably even the Lower Silurian. *Nodosariæ* and *Dentalinæ* abound in some of the Permian limestones of Durham and the Wetterau in company with *Textulariæ*. *Nodosaria* occurs also in the Carboniferous Limestone of Ireland, according to M'Coy; and the green sand of the Lower Silurian series near St. Petersburg has granted to Ehrenberg casts of chambers something like those of *Dentalina*, together with unmistakeable casts of Textularian and Rotalian shells. We may remark, too, that the *Fusulina* of the Russian, North American, and Arctic Mountain limestone carries back the pedigree of the *Nonionina* group to the palæozoic periods, and that it is accompanied with other Foraminifera of known types, among which *Nummulina* is not absent. This last-named type has rare representatives in the Lias and Oolite; it acquired great potency in the Tertiary seas, and is not extinct now.—Altogether we have here some remarkable instances of the persistency of life-types among the lower animals. Though the specific relations of the Palæozoic Forami-

* Quarterly Journal of the Geological Society, August 1860, p. 294.

nifera require further elucidation, we feel certain that the six genera represented in the Upper Triassic clay of Chellaston by about thirty varieties, stand really in the place of ancestral representatives of certain existing Foraminifera, that they put on their several subspecific features in accordance with the conditions of their place of growth, just as their posterity now do, and that although we have in this instance met with only the minute forms of a 700-fathoms mud-bottom, yet elsewhere the contemporaneous fuller development of these specific types may be found by careful search in other and shallower-water deposits of the Trias period*."

259. It can scarcely, I think, be questioned that such a continuity of the leading types of Foraminifera maintained through so long a series of geological periods, and the recurrence of similar varietal departures from those types, are results of the facility with which creatures of such low and indefinite organization adapt themselves to a great variety of external conditions; so that, on the one hand, they pass unharmed through changes in those conditions which are fatal to beings of higher structure and more specialized constitution; whilst, on the other, they undergo such modifications under the influence of those changes, as may produce a very wide departure from the original type. Thus we have found strong reason for regarding temperature as exerting a most important influence in favouring not merely increase of size but specialization of development: all the most complicated and specialized forms at present known being denizens either of tropical or of sub-tropical seas; and many of these being represented in the seas of colder regions by comparatively insignificant examples, which there seems adequate reason for regarding as of the same specific types with the tropical forms, even though deficient in some of their apparently most important features. The depth of the sea-bottom seems also to affect the prevalence of particular types, and to modify the forms under which these present themselves; so that Messrs. Rupert Jones and Parker feel themselves able to pronounce approximatively as to the depth of water at which a deposit of fossil Foraminifera may have been formed, by a comparison of its specific and varietal types with those characterizing various depths at the present time. And it is specially worthy of note, that in the greatest depths of the ocean from which Foraminifera have been brought by deep-sea soundings, these belong almost exclusively to one type, *Globigerina*.

260. In applying the results of the foregoing inquiry to the Animal Kingdom generally, it may be at once conceded that no other group affords anything like the same evidence, on the one hand of the derivation of a multitude of distinguishable forms from a few primitive types, and on the other of the continuity of those types through a vast succession of geological epochs. But a nearly parallel case, as regards the first of these points, is presented by certain of the humbler groups of the Vegetable Kingdom; in which it is becoming more and more apparent, from the careful study of their life-history, not only that their range of variation is extremely wide, but that a large number of reputed genera and species have been erected on no better foundation

* Quarterly Journal of the Geological Society, November 1860, p. 458.

than that afforded by the transitory phases of types hitherto known only in their states of more advanced development*. It would be very unreasonable to put aside these cases as so far exceptional that no inferences founded upon them can have any application to the higher forms of Animal and Vegetable life. For it is only in the *degrees* of their range of variation, that *Foraminifera* and *Protophyta* differ from *Vertebrata* and *Phanerogamia*; and the main principle which must be taken as the basis of the systematic arrangement of the former groups,—that of ascertaining the range of variation by an extensive comparison of individual forms,—is one which finds its application in every department of Natural History, and is now recognized and acted on by all the most eminent Botanists and Zoologists. It will be sufficient for me here to refer to the views recently advanced by Dr. J. D. Hooker in his "Introduction to the Flora of Australia;" the results of his extensive experience in the comparison of the Floras of different portions of the globe having led him to conclusions regarding the probable origin of the diversities they present, with which my own deductions from the study of the Foraminifera are in complete accordance. And I am authorized by Mr. Thomas Davidson, whose extensive knowledge of the *Brachiopoda* enables him to speak as the highest authority upon all that relates to that most interesting group (which, like the Foraminifera, is traceable through the entire series of fossiliferous rocks), to state that in proportion to the increase of his knowledge of its modifications of type, does he find reason to regard many of them as having had so wide a range of variation, as fully to justify him in making a large reduction in the number of specific types hitherto accounted distinct; whilst in the same proportion he finds himself able to trace with considerable probability the same specific types through a succession of geological periods,—certain Oolitic and Cretaceous *Terebratulidæ*, for example, being the probable ancestors of existing forms; and even the *Lingula* of the Wenlock Silurians not being distinguishable by any characters which he can recognize as constituting a valid specific difference from the *Lingula anatina* of our present seas.

261. The following are the general propositions which it appears to me justifiable to base on the researches of which I have now given a *résumé*:—

I. The range of variation is so great among *Foraminifera*, as to include not merely the differential characters which systematists proceeding upon the ordinary methods have accounted *specific*, but also those upon which the greater part of the *genera* of this group have been founded, and even in some instances those of its *orders*.

II. The ordinary notion of *species* as assemblages of individuals marked out from each other by definite characters that have been genetically transmitted from original prototypes similarly distinguished, is quite inapplicable to this group; since even if the limits

* It is among the lower *Fungi* that the researches of Tulasne and others have shown the greatest variability to prevail; whilst the recent inquiries of Dr. J. Braxton Hicks have brought to light a most unexpected relationship between the supposed *Unicellular Algæ* and the *Gonidia* of *Lichens*. See his Memoirs in the Quarterly Journal of Microscopical Science, October 1860 and January 1861.

of such assemblages were extended so as to include what would elsewhere be accounted genera, they would still be found so intimately connected by gradational links, that definite lines of demarcation could not be drawn between them.

III. The only natural classification of the vast aggregate of diversified forms which this group contains, will be one which ranges them according to their direction and degree of divergence from a small number of principal family types; and any subordinate groupings of genera and species which may be adopted for the convenience of description and nomenclature, must be regarded merely as assemblages of forms characterized by the nature and degree of the modifications of the original type, which they may have respectively acquired in the course of genetic descent from a common ancestry.

IV. Even in regard to these family types, it may fairly be questioned whether analogical evidence does not rather favour the idea of their derivation from a common original, than that of their primitive distinctness.

V. The evidence in regard to the genetic continuity of the *Foraminifera* of successive geological periods, and of those of the later of these periods and the existing inhabitants of our seas, is as complete as the nature of the case admits.

VI. There is no evidence of any fundamental modification or advance in the Foraminiferous type from the Palæozoic period to the present time. The most marked transition appears to have taken place between the Cretaceous period, whose Foraminiferous fauna seems to have been chiefly composed of the smaller and simpler types, and the commencement of the Tertiary series, of which one of the earliest members was the Nummulitic Limestone, which forms a stratum of enormous thickness that ranges over wide areas in Europe, Asia, and America, and is chiefly composed of the largest and most specialized forms of the entire group. But these were not unrepresented in previous epochs; and their extraordinary development may have been simply due to the prevalence of conditions that specially favoured it. The Foraminiferous fauna of our own seas probably presents a greater range of variety than existed at any preceding period; but there is no indication of any tendency to elevation towards a higher type.

VII. The general principles thus educed from the study of the Foraminifera, should be followed in the investigation of the systematic affinities of each of those great types of Animal and Vegetable form, which is marked out by its physiological distinctness from the rest. In every one of these there is ample evidence of variability; and the limits of that variability have to be determined by a far more extended comparison than has been usually thought necessary, before the real relations of their different forms can be even approximatively determined.

VIII. As it is the aim of the Physical Philosopher to determine "what are the fewest and simplest assumptions, which being granted, the whole existing order of nature would result*," so the aim of the philosophic Naturalist should be to determine how small a number of primitive types may be reasonably supposed to have given origin by the ordinary course of "descent with modification" to the vast multitude of diversified forms

* Mill's Logic, 3rd edition, vol. i. p. 327.

that have peopled the globe in the long succession of geological ages, and constitute its present Fauna and Flora.

[*Note.*—I cannot bring to a conclusion this series of Researches, without on the one hand gratefully acknowledging the liberality of the Council of the Royal Society, whose assistance (from the Grant placed at their disposal by Government) has greatly aided my investigations, by enabling me to have every important feature of form and structure accurately delineated under a sufficient magnifying power; and, on the other, expressing my great obligation to the skill, intelligence, and patient assiduity of my draughtsman, Mr. GEORGE WEST, by whose careful study of these organisms under my direction I have been enabled to attain a much more thorough knowledge of their nature than my own more limited time would have permitted me to acquire.]

EXPLANATION OF THE PLATES.

PLATE XVII.

With the exception of figs. 9 and 10, all the figures in this Plate refer to *Polystomella craticulata*.

Fig. 1. *Polystomella craticulata*, as viewed at *a* in its peripheral aspect, showing the septal ridges and the intermediate rows of 'fossettes,' and, on the left of the figure, the septal plane with the row of minute apertures along its inner margin; at *b* is shown one of the lateral surfaces of the same shell, over the central part of which the septal ridges are concealed by an exogenous deposit that is irregularly dotted with punctations resembling the 'fossettes.' Magnified 10 diameters.

Fig. 2. Vertical section passing nearly through the umbilical axis, and laying open the outer seven whorls, but passing by those of earlier formation, so as to bring into view at *e* the external surface of the eighth (counting inwards). This figure shows the gradual increase of the distance between the two lateral surfaces of the successive whorls, of which those last formed do not invest the earlier, so that the shell would be biconcave but for the large amount of solid exogenous deposit, which not only occupies the umbilical region, but extends even to the last whorl; it also shows the continuity of this deposit with that outer portion of the spiral lamina of each whorl which presents in section a plicated aspect; and along the inner margin of each of the septa displayed in the section, is seen a row of minute septal pores, forming the only direct communication between the chambers. The relations of the various parts of the canal-system are well displayed in this section: *a*, *a*, the openings of the successive turns of one of the spiral canals transversely divided; *b*, *b*, the meridional canals, one

of which passes between each chamber and the one that succeeds, opening at each end into the spiral canal; *e*, the straight canals which come off from the spiral canals into the solid umbilical deposit, and pass through it direct to the external surface; *d*, the converging canals, which pass inwards from the meridional canals in the intraseptal spaces; *e*, the surface of the innermost whorl displayed by this section, on which are seen the meridional canals giving off their diverging branches in pairs. Magnified 30 diameters.

Fig. 3. Central portion of a section passing through the median plane of a specimen remarkable for the very *small* size of the primordial segment. Magnified 60 diameters.

Fig. 4. Central portion of a section (viewed under the same magnifying power as the preceding) passing through the median plane of a specimen remarkable for the very *large* size of its primordial segment. Magnified 60 diameters.

Fig. 5. Central portion of a section parallel to the median plane, but a little above it, showing one of the spiral canals and the central system of lacunæ in which it originates. Magnified 60 diameters.

Fig. 6. Portion of a section taken in a direction parallel to the median plane but much nearer the surface, showing parts of the canal-system of the outer whorls: *a*, *a*, portion of one of the spiral canals; *b*, *b*, portion of the succeeding whorl of the same canal; *c*, *c*, meridional canals of the inner whorl; *c'*, *c'*, origins of the meridional canals of the outer whorl, with their first pairs of diverging branches; *d*, *d*, origins of the canals that penetrate the solid umbilical deposit, which soon change their course and become vertical; *e*, transverse sections of vertical canals. Magnified 80 diameters.

Fig. 7. Marginal portion of a section taken in the same direction as fig. 2, and passing, in the whorls *a*, a^1, a^2, through the cavity of the chambers, whilst in the alternate whorls *b*, b^1, b^2, it passes along the septal plane; at *c*, *c*, are seen the meridional canals transversely divided near the points at which they give off their diverging branches. Magnified 60 diameters.

Fig. 8. Portion of a section taken through the median plane, showing the alternate position of the chambers *b*, *b*, *b*, with reference to those *a*, *a*, *a*, of the interior whorl, and those *c*, *c*, *c*, of the exterior whorl; at *d*, d^1, and d^2, are seen the external orifices of the diverging branches of the canal-system; and at *e*, *e'* are seen the junctions at their orifices of the adjacent branches of two distinct pairs, such junctions being generally connected with the septal apertures occupied by stolons of sarcode. Magnified 60 diameters.

Fig. 9. Section of *Polystomella crispa*, taken through the umbilical axis: *a*, *a'*, solid umbilical deposit; *b b*, *b' b'*, transverse sections of the two spiral canals; *c*, c^1, c^2, portions of the meridional canals; *d*, cæcal diverticula for the 'retral processes'; *e*, septal apertures. Magnified 50 diameters.

Fig. 10. Portion of a section of *Polystomella crispa* taken through the median plane,

and showing at a, a, a, the cæcal diverticula for the retral processes, and at b, b, the meridional canals transversely divided. Magnified 60 diameters.

Fig. 11. Portion of a section of *Polystomella craticulata* taken in the same direction as that represented in fig. 2, and showing the origin of the canals which pass vertically through the solid umbilical nucleus, and whose external orifices are seen at c, from the successive turns b, b, b of the spiral canal, which are seen transversely divided at a. Magnified 80 diameters.

Fig. 12. Portion of a section which has passed close to the lateral surface of one of the outer whorls, in such a manner as to show a portion of its spiral canal, with four of the meridional canals passing down the intraseptal spaces, and giving off successive pairs of diverging branches; between the septa from which they proceed is seen the finely-tubular substance forming the proper wall of the chambers. Magnified 80 diameters.

Fig. 13. Portion of a section passing through the median plane of the outer whorl, showing some minute shells of the foraminiferous type in the cavity of three of the chambers. Magnified 100 diameters.

PLATE XVIII.

The figures in this Plate refer to *Polystomella craticulata*, and to *Tinoporus baculatus*.

Fig. 1. Ideal representation of a specimen of *Polystomella craticulata*, laid open to show its internal structure: a, a^1, a^2, chambers of three whorls which are laid open by the plane of section; b, b^1, b^2, b^3, septa of four whorls alternating with the preceding, which are traversed by the plane of section; c, c^1, c^2, septal apertures; dd', dd', dd', meridional canals; e, e, e, and e', e', e', orifices of the successive turns of the two spiral canals (of which the upper one is displayed by the supposed removal of the umbilical nucleus) transversely divided; f, f, converging canals, passing inwards from the meridional canals; gg', gg', gg', surface of the last-formed portions of the spiral lamina, showing a row of furrows passing across between the septal bands, into which the diverging canals open in immediate contiguity to the septal bands; hh', hh', older portion of the spiral lamina, showing the replacement of each series of furrows by two rows of punctations; ii', ii', surface of the interior whorl, showing the obliteration of the septal bands and the rows of dimpled depressions into which the diverging canals open.

Figs. 2, 3, 4, 5. External aspect of specimens of *Tinoporus baculatus* from Borneo and Australia, showing the irregularity of their radiating prolongations. Magnified 20 diameters.

Fig. 6. A specimen of the same more enlarged, showing the areolated character of the surface of the disk, with elevated tubercles disposed between the areolæ, and

the furrowed surface of the terminal portion of the radiating prolongations. Magnified 40 diameters.

Figs. 7, 8, 9, 10. Specimens of the Philippine variety of *Tinoporus baculatus*, showing the variability of their form. Magnified 12 diameters.

Fig. 11. Fragment of *Polystomella craticulata*, showing the furrowed internal surface of three of the chambers, a, a^1, a^2, the furrows being deepest at the posterior margin for the reception of the retral processes; whilst at bb^1, bb^2, are shown two of the meridional canals laid open by the fracture of the septa which contained them, with the series of orifices of the diverging canals which pass off beneath the ridges that intervene between those furrows. Magnified 40 diameters.

Fig. 12. Internal cast of the chambers and canals of *Polystomella craticulata*, representing the form of the body and the distribution of the canal-system: a, retral processes, proceeding from the posterior margin of one of the segments; b b', smooth anterior margin of the same segment; c, c', stolons connecting successive segments, and uniting themselves with the diverging canals*; d, d^1, d^2, three turns of one of the spiral canals; e, e^1, e^2, three of the meridional canals; f, f^1, f^2, their diverging branches. Magnified 40 diameters.

Fig. 13. Fragment of a similar cast, showing a portion of three segments on their internal aspect, with their connecting stolons, c, two of the meridional canals, ee', and their diverging branches f, f. Magnified 40 diameters.

PLATE XIX.

All the figures in this Plate refer to *Calcarina Spengleri*.

Fig. 1. Disk of Philippine variety, as seen on the side nearest the apex of the spire, with the origins of the spines; showing the minute punctations and scattered tubercles of the surface of the disk, and the furrowed surface of the spines; the spire not anywhere apparent. Magnified 20 diameters.

Fig. 2. Disk of Maltese variety, as seen on the same side, showing the entire length of the spines, which in this specimen are unusually numerous and tend to subdivide at their extremities; no markings of any kind are seen on its surface, nor is the spire in the least apparent. Magnified 20 diameters.

Fig. 3. Disk of Philippine variety, as seen on the same side, with the origins of the spines, showing the punctations of the disk and the furrowing of the spines, with an unusual abundance of semitransparent tubercles; the spire not anywhere apparent. Magnified 20 diameters.

* This portion of the figure is ideal; and by a misapprehension on the part of the artist, the segments of the inner whorl have been made to range with those of the outer whorl, instead of alternating with them which seems to be the typical arrangement, though often departed from.

Fig. 4. Disk of Philippine variety, as seen on its growing side, with the origins of the spines; the last half whorl is here apparent, the newest chambers having only their own proper walls, whilst those which preceded them are more and more overgrown by the 'intermediate skeleton,' in which they gradually become imbedded; the surface of the disk shows the usual punctation, with an average development of tubercles; that of the spines is furrowed. Magnified 25 diameters.

Figs. 5, 6, 7. Young *Calcarinæ*, showing their ordinary aspect. Magnified 20 diameters.

Figs. 8, 9. Hispid varieties of Philippine *Calcarinæ* (see also Plate XX. fig. 6). Magnified 30 diameters.

Figs. 10, 11. Portions of figs. 8 and 9 more highly magnified: in fig. 10 it is seen that the spines are tubular, being formed around the pseudopodia as they issue from the passages in the shell. Magnified 60 diameters.

Fig. 12. Ideal representation of *Calcarina* laid open; showing the unsymmetrical or 'turbinoid' disposition of the spire (its apex being placed downwards for more convenient display); the Rotaline aspect of the last-formed chambers, and the row of pores along the inner margin of the septal plane, which constitutes the only aperture of the last chamber; the manner in which each turn of the spire is overgrown by the exogenous deposit forming the 'intermediate' or 'supplemental skeleton' which fills up the whole interior of the cone, and conceals all but the last-formed portion of the spire; the penetration of this 'supplemental skeleton' by canals, which originate on the outside of the proper walls of the chambers, and pass in a somewhat radiating direction towards both surfaces of the disk, separated at intervals by non-canaliferous cones, whose bases appear externally as elevated tubercles; the connexion of the spines with the 'supplemental skeleton,' from which the older spines receive new investments at every turn of the spire; and the extension of the canal-system into the spines, on the furrowed depressions of whose surface it opens at numerous points.

PLATE XX.

All the figures in this Plate refer to *Calcarina Spengleri*.

Fig. 1. Section of the disk taken through the axis of the spire: a, a^1, a^2, a^3, a^4, successive whorls transversely divided; b, the proper wall of the last-formed chamber, not yet consolidated by exogenous deposit; c, row of pores at the inner edge of the septal plane, constituting the only communications between the chambers; d, d, canals passing through the supplemental skeleton to the surface of the disk; e, e, non-canaliferous portions of the supplemental skeleton. Magnified 50 diameters.

Fig. 2. Portion of a section taken through the inner whorls, transversely to the axis of the spire; showing the commencement of the canal-system in central lacunæ from which a spiral extension may be traced that gives off branches proceeding into one of the spines; and showing the free inosculation of these branches in the substance of the spine with others derived from the nearest chambers, so that the entire substance of the spine is minutely intersected by them. Magnified 50 diameters.

Fig. 3. More enlarged portion of a section passing through the 'supplemental skeleton' in the immediate neighbourhood of the surface of one of the chambers; showing the freedom with which it is traversed by the canals. Magnified 100 diameters.

Fig. 4. Section of the disk taken through the later whorls, transversely to the axis of the spire: *a*, central lacunæ of the canal-system excavated in the portion of the intermediate skeleton overlying the primordial chamber; a^1, a^2, a^3, a^4, successive whorls; *b*, b^1, b^2, the proper walls of the chambers of the last whorl, receiving successive increments in thickness from exogenous deposit; *c*, *c*, septal apertures; *d*, d^1, d^2, d^3, the 'supplemental skeleton' of the last whorl, showing its progressive increments in thickness; *e*, e^1, e^2, e^3, e^4, e^5, the spines in order of age, as determined by the portion of the supplemental skeleton from which they are outgrowths. Magnified 50 diameters.

Fig. 5. Section of a portion of the 'supplemental skeleton' taken near the surface of the disk, in a direction transverse to the axis of the spire, showing the distribution of the orifices of the canals around the non-canaliferous spaces *e*, *e*, *e*. Magnified 100 diameters.

Fig. 6. A young specimen of the hispid variety (see Plate XIX. figs. 8, 9). Magnified 30 diameters.

Fig. 7. Section of a young *Calcarina*, taken transversely to the axis of the spire, showing at *a* and elsewhere a diverging arrangement of the branches of the canal-system analogous to that of *Polystomella*. Magnified 60 diameters.

Fig. 8. Section of a young specimen of the hispid variety taken in the same direction. Magnified 60 diameters.

PLATE XXI.

All the figures in this Plate refer to *Tinoporus*.

Fig. 1. External view of a conical specimen of *T. lævis*, as seen laterally at *a*, and on its basal aspect at *b*. Magnified 25 diameters.

Fig. 2. Section of *T. lævis* in a direction parallel to the base, showing an irregularly concentric arrangement of chambers, the floors of which are perforated with numerous foramina. Magnified 50 diameters.

Fig. 3. Section of *T. lævis* in the direction of the axis of the cone; showing at *a* the spherical primordial chamber, and at *b* and *c* the chambers first connected with it on either side; showing also the manner in which the successively-formed chambers are piled upon one another vertically, with the large lateral orifices of communication between the adjacent chambers. Magnified 50 diameters.

Fig. 4. Ideal representation of a portion of *T. lævis*, to show the relations of the chambers, which are divided from one another horizontally by cribriform floors, and laterally by walls in which there are large apertures *a*, *a*, *a*, leading into the adjacent chambers.

Fig. 5. Section of the basal portion of one of the radiating outgrowths of *T. baculatus* (Plate XVIII. fig. 6), showing the manner in which the chambers are clustered around the solid axis, and in which the axis (a portion of the supplemental skeleton) is traversed by canals radiating from its centre to its circumference. Magnified 50 diameters.

Fig. 6. Section of the Philippine variety of *T. baculatus* (Plate XVIII. fig. 7), taken through its median plane, showing the mode in which the intermediate skeleton is interposed among the chambers, so as to constitute the axis of the radiating outgrowths. Magnified 25 diameters.

Fig. 7. Section of *T. baculatus*, taken in the direction perpendicular to its median plane; showing an arrangement of its chambers essentially corresponding to that exhibited on a larger scale in fig. 3; the piles of chambers partially separated, however, from each other by the interposition of the solid columns of the 'intermediate skeleton.' Magnified 40 diameters.

Fig. 8. Portion of a section of *T. baculatus*, taken (as fig. 2) parallel to the median plane, but near the surface; showing the greater thickness of the walls of the chambers, and the interposition of the solid columns transversely divided at *a*. Magnified 50 diameters.

Fig. 9. Portion of a section of the Philippine variety of *T. baculatus*, more enlarged, to show the canal-system, *b*, *b*, traversing the thick walls of the chambers. Magnified 100 diameters.

Fig. 10. Portion of the section represented in fig. 6, more enlarged, showing, at *a*, *a*, a portion of the solid axis of one of the radiating outgrowths, traversed by the canals, *b*, *b*, and invested by two layers of chambers, the walls of which are rendered hispid by spinous excrescences. Magnified 100 diameters.

Fig. 11. Section of the central portion of a specimen of *T. baculatus*, passing through the median plane; showing at *a* its regularly spiral commencement (not distinguishable from that of a *Calcarina*), the origin of the spines from the intermediate skeleton of the spire, and the early exchange of the spiral type for an irregular clustering of the chambers, as shown at *b*. Magnified 80 diameters.

PLATE XXII.

All the figures in this Plate refer to *Carpenteria*.

Fig. 1. Portion of a group of *Carpenteriæ* growing upon the surface of *Porites* (coral); a part of the external wall of the uppermost specimen having been thinned-away by acid, so as to show the areolation of its inner surface. Magnified 5 diameters.

Figs. 2, 3, 4. Interior of the first-formed chambers of three specimens, showing their Globigerine characters and arrangement; at *a*, *a*, are shown the remains of the yellowish-brown spongeous substance by which those chambers were occupied. Magnified 50 diameters.

Fig. 5. Isolated specimen of *Carpenteria* on the shell of *Pecten*, in which the chambers of the last whorl diverge so widely at the base of the cone, as to be in great degree separated from each other. Magnified 5 diameters.

Fig. 6. Portion of the external wall, showing the areolated aspect it derives from the gentle convexities into which it rises between the reticulations that project on its internal surface; at *a* is shown the natural external surface on which the foramina are regularly disposed; at *b* that surface has been removed by grinding, so as to bring into view the inner layer of the wall, on which the foramina are seen to be deficient along the projecting ribs, but to be more closely set together in the portions surrounded by these (see fig. 15). Magnified 30 diameters.

Fig. 7. Section of a very flat specimen, parallel to the base of its cone, but not far from its apex; showing at *a* the vertical funnel transversely divided, at *b* its communication with the last chamber, at *c* its communication with the penultimate chamber, at *d*, d^1, and d^2 three of the complete septa dividing the principal chambers, and at *g* and g^1 portions of the canal-system. In some of the chambers are seen spicules resembling those of Sponges. Magnified 20 diameters.

Fig. 8. Portion of a specimen partially laid open by grinding away the apical portion of the cone: *a*, *b*, *c*, *d*, as in the last figure; *e*, e^1, e^2, secondary septa partially dividing the principal chambers, but not extending to their central portion; *f*, f^1, f^2, incomplete septa projecting inwards from the external wall, but not crossing the cavity of the chamber to reach the opposite wall. Magnified 20 diameters.

Fig. 9. Portion of the upper part of the specimen represented at the top of fig. 1, much more enlarged, showing the reticulated arrangement of those incomplete septa; the spaces included in the reticulations are in some instances covered-in by a thin layer of the shelly wall which has not been removed; but in most other cases this wall has been eaten away by the acid in the central

portion of the reticulation, so as to display the dark spiculiferous substance within. Magnified 30 diameters.

Fig. 10. Portion of the group of *Carpenteriæ* growing on the surface of *Porites*, of the natural size.

Fig. 11. An unusually large specimen, of the actual size.

Fig. 12. Portion of a section taken in the same direction as fig. 7, but represented on a larger scale, showing the annulations of the foramina that are seen obliquely traversing the shell, and the two layers, of which not only the principal septa *a*, *a*, but also the incomplete septum *b*, are formed, with the canals included between them. Magnified 75 diameters.

Figs. 13, 14. External apertures at the apex of the cone of two specimens, showing their peculiarly Milioline character. Magnified 20 diameters.

Fig. 15. Section traversing the external wall of one of the chambers perpendicularly to its surface, showing at *a*, *a*, the annulated foramina by which it is traversed, and at *b*, *b*, *b*, sections of the imperfect septa, on which the foramina do not open. Magnified 75 diameters.

Fig. 16. Siliceous spicules (resembling those of *Halichondria*) from the spongeous tissue occupying the chambers of *Carpenteria*. Magnified 75 diameters.

XXVI. *Researches on Sugar Formation in the Liver.* By Frederick William Pavy, *M.D.* *Communicated by Dr. Sharpey, Sec. R.S.*

Received June 21,—Read June 21, 1860.

The following communication is an abridgement of a paper on the same subject presented to the Royal Society in 1858, with some additional matter that has been since disclosed by my experimental investigations. The original paper, being deposited in the Archives of the Society, is accessible for reference on points of detail that are here excluded.

In 1848 it was announced by Bernard that the liver enjoyed a sugar-forming function. This statement appeared to rest upon irrefutable grounds, and the new function soon became almost universally acknowledged by physiologists. An animal which had been for some time previously restricted to an animal diet was suddenly killed. Sugar was found abundantly in the blood of the *vena cava* and hepatic veins, whilst none existed in that of the portal vein. The tissue of the liver was also found abundantly saccharine, whilst no sugar was to be detected in any other organ. I had seen this experiment several times performed in Bernard's laboratory, and had often repeated it myself. From the correctness of the description of his results, I entertained no doubt as to the accuracy of Bernard's deductions, and did not for a moment seek to question them. In the course of my experimental research, however, I was conducted step by step to a point which has placed me, involuntarily as it were, in antagonism with the glycogenic theory. By pushing investigation further than had hitherto been done, I have been compulsorily brought to arrive at conclusions of which I had not the most remote anticipation beforehand.

More recently the existence of a material, allied in its nature to starch, has been discovered in the liver which has been looked upon as destined for transformation into sugar. This "amyloid substance" has been hence called by Bernard the glycogenic matter. The discovery of this substance did not alter his pre-existing views, but simply provided a recognizable source for animal sugar.

The question arising out of my experimental results to be mentioned, is not whether sugar can be formed in the animal system independently of a saccharine alimentation, but whether the sugar so largely met with in the liver and a certain portion of the blood after death by the hitherto adopted processes of examination is to be taken as representing an *ante-mortem* or physiological condition; and whether the liver enjoys the special sugar-forming function that has been assigned to it.

It was upon finding that blood withdrawn from the right side of the heart during life differed so much in the amount of sugar it contained from what had been inferred

from examination on removal after death, that I was led to inquire into the substantiality of the glycogenic theory. From the experiments I had seen performed in Paris, and those I had made myself, I had regarded the blood of the right side of the heart as naturally strongly charged with sugar. When collected without the observance of certain precautions, from the hepatic veins, inferior cava, right auricle, or right ventricle of the recently killed animal, the blood, after the usual preparation for analysis with the sulphate of soda, gives a copious yellow or orange-yellow reduction on being tested with the copper solution, and this was looked upon as representing the state belonging to life. In February 1854 I was led in some experiments I was then conducting, to draw blood by a catheter from the right ventricle of the living animal, and was astonished to find that the blood removed did not present what I had hitherto looked upon as the natural reaction of right ventricular blood, for it was scarcely at all impregnated with saccharine matter. In June of the same year, according to my note-book, I again removed blood from the right ventricle during life, and observed it to contain scarcely a trace of sugar; whilst, on the animal being immediately afterwards killed, the blood which flowed from an incision into the right heart gave the usual reduction with the Barreswil solution.

Notwithstanding that such results appear now so striking, yet I did not at first give to them their proper significance. My mind was so strongly impressed with the prevailing conviction that sugar was extensively formed by the liver during life and poured into the circulation through the hepatic veins, that I felt inclined to think the catheter had not been fairly introduced into the heart, or had come in contact with the current of blood descending through the superior cava, rather than discredit our previous notions, and no longer regard the strongly saccharine state of the blood met with so soon after death, as a representation of its natural or *ante-mortem* condition.

This question afterwards presenting itself strongly before me, I was anxious definitely to decide if death really occasioned an alteration, as to the presence of sugar, in the blood escaping from the liver. Such an effect, as far as I am aware, had never been spoken of, or even hinted at by others. Several experiments were performed with the greatest care. Blood was withdrawn from the heart during life by the introduction of a catheter, and immediately afterwards the life of the animal was destroyed and blood collected by a free incision into the auricle or ventricle. In two cases the catheter had perforated the heart, and the blood that was removed during life had escaped into the pericardium, thus placing beyond all doubt, that a fair sample had been obtained. In every experiment (and the experiments were most numerous) the result of the examination of the blood was the same. The blood yielded by the right heart during life, gave only the merest trace of saccharine reaction, no more than was met in the arterial system; whilst that which was collected after death reduced abundantly the copper solution.

In some experiments a quantitative determination of the sugar existing in the blood collected from the right side of the heart after death was made, and the following are the results that were obtained.

Blood from the carotid artery and from the right ventricle during life.	Blood (defibrinated) from the right side of the heart after death.	Liver a short time after death.
No. 1. Trace of sugar.	$\frac{7}{10}$ths gr. of sugar per cent.	Not analysed.
No. 2. Trace of sugar.	$\frac{65}{100}$ths gr. of sugar per cent.	4·10 grs. of sugar per cent.
No. 3. Trace of sugar.	$\frac{5}{10}$ths gr. of sugar per cent.	3·39 grs. of sugar per cent.
No. 4. Trace of sugar.	$\frac{94}{100}$ths gr. of sugar per cent.	2·45 grs. of sugar per cent.
No. 5. Trace of sugar.	$\frac{7}{10}$ths gr. of sugar per cent.	2·44 grs. of sugar per cent.

At the time the above analyses were made, I looked upon the amount of sugar in the right ventricular blood removed during life as too small for exact determination. I have since, however, found that although minute, yet, the quantity is with care susceptible of being ascertained. Defibrinated blood is poured into spirit, and the precipitate thoroughly washed with that agent. The filtered liquid is evaporated to a small bulk, and the sugar then estimated with the Barreswil solution. The following figures may be given as affording an average representation of the per-centage of sugar normally existing in living right-ventricular blood of the dog, for the specimens taken behaved, as regards degree of reaction, like those belonging to the extensive number of examinations that I have made.

Blood collected six hours after a meal of animal food; 710·1 grs. of defibrinated blood taken for analysis: sugar $\frac{47}{1000}$ths of a grain per cent.

Blood collected twenty-four hours after the last food had been given: sugar $\frac{73}{1000}$ths of a grain per cent.

Blood collected $4\frac{1}{2}$ hours after a copious meal: sugar $\frac{88}{1000}$ths of a grain per cent.

It is therefore evident that blood collected from the right heart, as has hitherto been done after death, affords an indication differing most essentially from that yielded by blood withdrawn from the same part during life. Consequently inferences of the *ante-mortem* state that have been drawn from *post-mortem* examinations must be abandoned.

With the knowledge we now possess, it is easy to operate and find the blood after death presenting the condition that is natural to life. When an animal is killed, and even only a short time is allowed to elapse before the chest is opened to collect the blood from the right heart, it is found strongly saccharine. But if life be instantaneously destroyed, and the chest as rapidly as possible opened, and the heart ligatured at its base and excised, then the contents of its right cavities will be found as free from sugar as if catheterism had been performed during life. Here the steps of the operation are so rapid that time is not given for the *post-mortem* effects on the liver and the circulating fluid to be manifested.

I think, perhaps, that this is even a preferable mode of operating; and if expeditiously performed, gives blood more free from sugar than after removal with the catheter during life. Very slight causes are sufficient to determine an increase of sugar in the circulation. Struggling on the part of the animal leads to compression of the liver by the abdominal parietes, and more or less congestion of the circulation, by interfering

with the freedom of the breathing. In resorting to catheterism of the heart, my experience is, that unless the animal has remained perfectly tranquil during the whole of the operation, the blood will give a decidedly stronger shade of saccharine indication than is obtained under a natural or tranquil state of the system.

According to the state of tranquillity or restlessness of the animal, I can predicate with confidence the condition its blood will present; and when the operation is unattended with the least attempt at resistance, which only happens occasionally, the amount of reaction is so small that it is liable to be overlooked altogether, unless special attention is given. It is for this reason that I can reckon with greater certainty on meeting with the blood of the right side of the heart in a perfectly normal state on suddenly killing the animal and instantly excising the heart, than on removal through the catheter during life.

This affords an explanation, why blood removed from the carotid artery immediately after exposing the vessel, is ordinarily found in a marked degree more saccharine than when collected ten minutes or so after the operation of exposing the artery has been effected. From the contiguity of the carotid artery to the pneumogastric nerve, picking up the vessel is almost universally attended with considerable struggling and disturbance of the breathing. But when the artery has been once fully separated from its adjacent structures and a ligature placed around it, it can be drawn out and blood collected without causing any fresh struggling or disturbance.

I have upon a few occasions found blood removed from the carotid artery giving a shade stronger reaction than the blood previously withdrawn from the right side of the heart. I consider this to have been due to the different effects of the respective operations required. Exposing the jugular and passing a catheter into the heart, is not so likely to occasion struggling and disturbance as exposing the carotid.

From some experiments I have recently performed, it would seem that the portal blood, instead of being entirely free from sugar, contains, as far as is discoverable by the behaviour of the blue liquid, the same amount that is met with under natural circumstances in the heart and other parts of the circulatory system. Blood is examined (certainly by myself) much more closely now, than when such a wide difference was considered to exist in it from different parts of the circulation. A trace of reaction is now looked for and noted that would have formerly passed over unobserved. For instance, on well-boiling a specimen derived from portal blood with the blue liquid, there is no reduction to be perceived. The test appears to have given no reaction, and such would have been formerly described as the result. Had the test-tube been placed aside, however, and examined again in the course of half an hour, just a traceable amount of red oxide would have been found, according to my recent experience, to have subsided. The following is the account of three consecutive experiments that I have lately performed, in which a careful comparative examination of the portal and cardiac blood was made. The dogs had been feeding on tripe for some days past. They were suddenly killed by pithing. The abdomen being instantly opened, a ligature was placed (observing the precautions mentioned by BERNARD) around the portal vein. The chest

was immediately afterwards laid open and the heart instantly excised, and the blood collected from its cavities. Both portal and cardiac specimens of blood behaved precisely as I have described above, namely, gave no perceptible reduction on boiling with the blue liquid, but occasioned a traceable amount of red oxide to collect on reposing for a short time. There was no recognizable difference in the amount of deposit produced by the respective specimens of portal and cardiac blood.

That obstruction to the breathing occasions an unnaturally increased amount of sugar in the circulation is not only proved by examination of the blood; but the amount may be so large as to lead to the production of a diabetic state of the urine. Thus, in a healthy dog at a period of digestion I have obtained the following result. The urine was first drawn off and tested, and gave no trace of reaction. The head was then muffled in a bladder for an hour, during which time the supply of air allowed was exceedingly limited. A state was induced just short of coma or unconsciousness, and when the bladder was removed the animal immediately revived. The urine after this operation gave an orange-yellow reduction with the copper solution.

Although the conclusions advanced in this communication stand in antagonism to the glycogenic theory of BERNARD, yet I consider there is only one essential point where our *experimental results* are at variance. It is not that the statements here brought forward contradict the accuracy of BERNARD's experiments. There is no doubt about the correctness of these experiments, and my own views are perfectly compatible with them. It is the inferences drawn from them that I contend are fallacious. A *post-mortem* condition has been taken as representing an *ante-mortem* or physiological state. At first there was no reason to suppose that this would occasion any error, but by the investigations I am detailing, it appears that the two are distinct from each other. And when BERNARD speaks of blood removed by the catheter from the right heart of the living animal precipitating "très nettement le sel de cuivre*," here my experience is directly opposed to him. If a most extensive number of observations enables me to speak with decision, I can confidently assert that such is not the normal character of blood contained in the heart during life.

At the time of discovering the fallacy of inferring the physiological state of the blood from the character it presented when collected from the heart after death, I still regarded the liver as strongly charged with sugar during life. I did not as yet think that the saccharine state of this organ displayed by our hitherto adopted mode of examining it was due likewise to a *post-mortem* occurrence. My first step was by injections of blood through the liver at different pressures, so as to imitate different states of the circulation, to endeavour to account for the sugar escaping so largely immediately after death whilst it scarcely appeared during life. Failing to discover anything decisive from these experiments, I began to direct my attention to the state of the liver tissue itself during life. I did not regard it as probable, but still, just possible, that the liver, like the blood coming from it, might be free, or almost entirely free, from sugar during life, and that

* Leçons de Physiologie, Paris, 1855, p. 121.

the presence of this principle might be due to some *post-mortem* change. Acting upon this idea, I resolved to see if I could not alight upon the organ in the state actually belonging to life, by placing it in a condition at the instant of death that would prevent any subsequent production of sugar.

The researches of BERNARD having disclosed the existence of a material in the liver which passes with great rapidity into sugar under the influence of ferments, I looked for an agent that might possess the power of preventing this transformation, without destroying the material or its product. Saliva is an exceedingly energetic ferment towards this substance, but I found that it ceased to exert any catalytic effect in the presence of an alkali. I therefore injected a strong solution of potash into the portal vein instantaneously after the destruction of life, with the view of preserving the liver in its natural state. After this operation, I have failed to detect any, or more than a mere trace of sugar in the substance of the organ; and it has been proved, by afterwards submitting a liver in which saccharine matter has existed, to a precisely similar process, that the injection has no effect towards leading to a decomposition of this principle. A saccharine liver injected with potash gives as copious a reaction as if the injection had not been practised.

Acids, like alkalies, check the action of ferments on this substance belonging to the liver, and a strong solution of citric acid injected into the portal vein has been observed to be followed by a similar effect to the injection of potash.

Although I believe that these experiments may be relied on as affording accurate information regarding the physiological state of the liver, yet a feeling of hesitation might possibly arise in accepting the results derived from the employment of a caustic alkali, when the subsequent recognition of an organic substance like sugar is concerned. There are other means, however, that enable us to display the condition of the liver belonging to life. The mere alteration of temperature is sufficient to effect the object that is desired. Processes of the nature of fermentation are checked by cold; and as the formation of sugar in the liver is of this character, the rapid abstraction of heat instantaneously after the destruction of life prevents any *post-mortem* change taking place, and presents us with the organ in a natural or physiological state.

The experiment showing the effect of reduction of temperature is thus performed. An animal is killed as quickly as possible by pithing the *medulla oblongata*. The abdomen is instantly opened by a free incision through its parietes, and a piece of the liver sliced off and plunged into a freezing mixture of ice and salt, which has stood sufficiently long to have become liquefied. If the ice and salt are used immediately after being mixed, and whilst still in a solid state, their cooling effects are not nearly so intense, and not sufficiently so for our purpose. The piece of liver in the course of a few minutes is frozen quite hard. It is taken out, cut up into thin slices, pounded to a pulp in a mortar, and placed, a little at a time, in a rather small quantity of water, which is kept thoroughly boiling during the process. The cold has merely checked the action of the ferment existing in the liver. The materials are there in an undestroyed state,

and a production of sugar takes place on the temperature being raised to a moderate extent. The object, therefore, is to apply the heat rapidly, so as to coagulate the albuminous principles and thus destroy the ferment. The decoction that is obtained gives none, or at the most the merest trace of reaction. It abounds in the sugar-forming substance, and on being treated with a little saliva and exposed to a moderate heat, a transformation is with an astonishing rapidity effected. The remainder of the liver that has been left in the animal is now submitted to the ordinary process of preparation, and tested, to show that it gives the usual reaction that was formerly thought to belong to it during life.

The rabbit is a more favourable animal for this experiment than the dog, because, on account of its size and the thinness of its abdominal parietes, the liver can be more quickly reached and a piece of it sliced off. Again, the liver of the rabbit is not so thick as that of the dog, and thus is more rapidly acted on throughout by the freezing mixture. I have often, in the case of the dog, found the moderately thick outside parings of a piece of frozen liver free, or almost completely free, from sugar, whilst the centre has given a tolerable saccharine reaction. The centre of a thick piece of liver may be found, even after immersion for some minutes, in a soft or unfrozen state; and when the abstraction of heat is only gradual, time is given for the production of a certain amount of sugar.

Whether the animal, either rabbit or dog, is at a period of digestion or not, makes no difference, that I have perceived, in the result. Usually my experiment has been made a few hours after food has been taken. A piece of healthy frozen liver that is free from sugar, on being raised for a few minutes to a temperature of 90° or 100°, gives a most copious saccharine reaction. A piece of saccharine liver plunged into a freezing mixture loses none of its saccharine qualities.

The result produced by boiling water on the liver is similar to that of a freezing mixture. It coagulates or destroys the materials capable of acting as ferments, and so prevents the ordinary *post-mortem* transformation from occurring. Its action, perhaps, is not quite so perfect as that of freezing, but still, especially with the liver of the rabbit, specimens are easily obtained yielding only the faintest indication of sugar. On testing the decoction, there is no change on boiling with the blue liquid, but after some time a few particles of red precipitate may subside. The animal is suddenly killed, and a piece of the liver as rapidly as is possible removed and thrown into a large quantity of boiling water. It need not remain more than two or three minutes. Pounded in a mortar with water and boiled, a liquid is furnished on filtration for testing.

It has been noticed by Bernard, that after division of the spinal cord just below the phrenic nerves, the liver is found free from sugar upon being ordinarily examined at the period of death, whilst it becomes strongly saccharine afterwards. Various suggestions have been made in explanation of this phenomenon. The fact itself is a most striking one, and has frequently been corroborated in my laboratory. It fully agrees with the experiments I have been mentioning, and receives from them, I consider, a satisfactory

explanation. After the division of the spinal cord, the temperature of the animal rapidly falls. In one case I noticed in a rabbit 3½ hours after the operation, that the temperature of the rectum was only 67°. This low degree of temperature at the time of death renders the *post-mortem* production of sugar so slow a process, that it is easily recognized in its true light.

Maintaining artificially the heat of the animal by exposure to a high temperature after division of the spinal cord, altogether alters the result. Thus, a rabbit in which the spinal cord had been divided just below the phrenics, was placed in an atmosphere where the thermometer stood at 88°. In three hours' time, when it was killed by pithing, the temperature of its rectum was 104°. The liver behaved precisely as if the animal had been suddenly killed in its ordinary state, sugar being found, after an ordinarily conducted examination, to its usual extent.

It has also not escaped the observation of BERNARD, in experimenting on the frog, that, according to the temperature of the animal at the time of death, the liver is found with or without sugar after an ordinarily conducted examination. In the 'Comptes Rendus' of the Academy of Sciences, March 1857, he mentions this fact, and refers it to a variation in the activity of the circulation, produced by the high and low temperature leading to an increase or decrease, or even arrest of the glycogenic function. I had obtained results corresponding with those of BERNARD before I was aware he had undertaken his experiments. Frogs in good condition, in which the liver is large, pale-coloured, and exceedingly rich in amyloid substance, were exposed for two hours to an atmosphere heated to 90°. An examination of the livers in the usual way afforded a decided indication of the presence of sugar. In other frogs, without exposure to the elevated temperature, the livers similarly examined gave no reaction with the Barreswil solution. Whilst repeating these experiments, I accidentally met with a result for which I was formerly at a loss to account. Some frogs that had been exposed to heat happened to be placed aside in my laboratory for a quarter of an hour before they were killed. Their livers, being examined, yielded scarcely an indication of a trace of sugar. Time had been given for the temperature to fall; and from what has preceded, it will now be seen that the absence or presence of sugar in these experiments depends upon the influence that a high or low temperature has been shown to exercise over the *post-mortem* change that occurs in the liver.

I have found the livers of the oyster and mussel, when these animals are in a fresh and healthy state, to be free from the presence of sugar. But the livers contain a large quantity of the amyloid substance, and should the animals have been allowed to die, or have been kept for some time, sugar may be encountered to a large extent. The same is the result when the livers are removed and moderately heated a short time before the examination is made.

Immediately underneath the shell of the mussel (*Mytilus edulis*) is a layer—the mantle—which is highly charged with the same amyloid substance that is met with in the liver. When the animal is in good condition, this layer is thick and opakely white

or yellowish; but when in the opposite state, it is thin, transparent, and watery. This mantle, of good-conditioned mussels, yields a decoction, which is quite milky from the amount of amyloid substance that is present. There is no sugar, and scarcely a proneness in the mantle itself to produce sugar; but if a ferment, such as a little saliva, be added, in a few moments an abundant production of sugar is the result.

The amyloid substance appears, from a micro-chemical examination of the liver, to be located in the hepatic cells. It belongs only to the healthy or physiological state, and may therefore be regarded as the result of a specific functional formation. It is most prone to descend by a chemical process into sugar; but an examination of the liver after different diets shows that it is produced, certainly in part, during life from sugar and its ally, starch.

In making a quantitative determination of this material in the liver, I have availed myself of its properties of resisting the action of a boiling solution of potash, and of being precipitated by spirit. The following results were obtained by pounding a piece of weighed liver with potash, adding a little water, and boiling some minutes until all was completely dissolved. The liquid was then poured into about six times its volume of spirit, by which the amyloid substance was thrown down as a white flocculent precipitate. The precipitate, after being well washed with spirit, was dried and weighed.

The size of the liver is to a most striking extent influenced by the nature of the diet; and the alteration that is thus induced is chiefly, if not entirely, due to the amount of amyloid substance present. I was first conducted to the discovery of these facts, whilst in my early experiments I was seeking to determine if the quantity of sugar found in the liver and blood of the dog after death was altered from its ordinary amount by the previous administration of a strictly vegetable diet. The process I then adopted for examining the liver was to remove and weigh it, and then to pass a stream of water through its vessels until its tissue was completely deprived of sugar. After a vegetable diet, I noticed, first, that the liver was of enormous size, in comparison with what I had been accustomed to meet with under an animal diet; and secondly, that there was a remarkable quantity of a material present which much interfered with my analysis, and which I subsequently found to be amyloid substance.

In all the observations that follow, the life of the animal was suddenly destroyed, its body then opened, and the liver removed. The liver thus circumstanced immediately drained itself, by the contraction of its vessels, of the principal portion of its blood, whereby was avoided those differences, as regards degree of congestion, which are observable in the human subject, where the examination is not made until some hours after death.

The observations are given without a single exception, just as they presented themselves under their separate heads; and further, the animals were taken, as they happened to be brought to me, without any selection, except such as was needed for the vegetable and saccharine diet, many dogs refusing to partake of this kind of food. The weights are of the avoirdupois scale. The dogs were weighed just before death, and

the weight of the liver is without the contents of the gall-bladder. Life was in most of the instances destroyed a few hours after the administration of food.

The Liver of the Dog under a Diet of Animal Food.

	Weight of dog.	Absolute weight of liver.	Relative weight of liver to animal.
	lbs. oz.	oz.	
No. 1 . . .	15 8	$7\frac{3}{4}$	1 to 32
No. 2 . . .	12 0	$7\frac{1}{4}$	1 to $26\frac{1}{3}$
No. 3 . . .	11 $14\frac{1}{3}$	$6\frac{1}{3}$	1 to 31
No. 4 . . .	15 10	$7\frac{3}{4}$	1 to 32
No. 5 . . .	11 0	$6\frac{1}{3}$	1 to 29
No. 6 . . .	11 $15\frac{1}{3}$	$6\frac{1}{3}$	1 to $29\frac{1}{3}$
No. 7 . . .	15 $5\frac{1}{3}$	$8\frac{3}{4}$	1 to 28
No. 8 . . .	24 $4\frac{1}{3}$	$11\frac{3}{4}$	1 to 33
No. 9 . . .	14 $9\frac{1}{3}$	$7\frac{1}{3}$	1 to 32
No. 10 . . .	17 0	$8\frac{1}{3}$	1 to $30\frac{1}{3}$
No. 11 . . .	9 8	$7\frac{1}{4}$	1 to 21
Total	158 $11\frac{1}{3}$	$85\frac{1}{4}$	1 to 30

The average of these eleven examples of dogs, restricted for some days prior to death to an animal diet, thus gives to the liver a weight equal to the $\frac{1}{30}$th part of that of the animal. Stating it in other words, there is very nearly half an ounce of liver for every pound the animal weighs.

Looking to the amount of amyloid substance present in these livers, my analyses have yielded the following results:—In seven out of the eleven examples, examinations were made under precisely similar circumstances. The liver was removed and weighed immediately after death, and a piece at once taken for analysis, so as to avoid more loss than was possible from *post-mortem* transformation into sugar.

Amount of Amyloid Substance in the Liver of the Dog after a Diet of Animal Food.

	per cent.
Example No. 3	8·29
Example No. 4	5·24
Example No. 7	5·61
Example No. 8	8·45
Example No. 9	4·88
Example No. 10	10·95
Example No. 11	6·94

Average amount of amyloid substance yielded by the above seven analyses 7·19 per cent.

The excluded examples are thus accounted for. In example No. 1 no analysis was made. In No. 2 the liver was left in the animal for $2\frac{1}{2}$ hours before it was examined.

It then yielded 3·37 per cent. of amyloid substance. In No. 5 the liver was left in the animal for ten minutes and then removed, but not examined for the space of two hours. It then yielded 3·51 per cent. of amyloid substance. In No. 6 an error occurred in the steps of the analysis, rendering it valueless.

The usual allowance for a dog in my laboratory is one of the ordinary penny bundles of tripe *per diem*. In examples Nos. 7 and 8 an extra allowance was given, to see if it occasioned any difference. To No. 7 was given two bundles of tripe daily for four days prior to its death. No. 8 was allowed its full tether, and the quantity of tripe it devoured was truly enormous; three bundles one day, four another, five the third, and two and a half the day it was killed. The figures yielded do not disclose any significant variation from the ordinary condition.

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To ascertain the effect of a vegetable diet on the liver, I submitted five dogs to a course of food for several days previous to death, consisting of barley meal and potatoes, or, where this was refused, to bread and potatoes. The following are the results obtained:—

The Liver of the Dog under a Diet of Vegetable Food.

	Weight of dog. lbs.	oz.	Absolute weight of liver. oz.	Relative weight of liver to animal.
No. 12	17	8	$19\frac{1}{4}$	1 to $14\frac{1}{2}$
No. 13	11	8	$12\frac{1}{2}$	1 to $14\frac{1}{2}$
No. 14	15	8	$11\frac{3}{4}$	1 to 21
No. 15	18	10	28	1 to $10\frac{1}{3}$
No. 16	17	5	$12\frac{1}{4}$	1 to $22\frac{1}{2}$
Total . . .	80	7	$83\frac{3}{4}$	1 to 15

Taking the average of these five instances as a sample of the effect of a vegetable diet on the liver of the dog, it appears that the organ rather more than equals in ounces the number of pounds the animal weighs. It will be remembered that, after an animal diet, the average given was rather under the half ounce to the pound. The facts as to the amount of amyloid substance stand thus:—

No analyses were made of the livers of the dogs Nos. 12 and 13, but the quantity of amyloid substance was unusually large. It was whilst examining these livers for the determination of sugar that I was first led to notice the effect of a vegetable diet that I am now describing.

Amount of Amyloid Substance in the Liver of the Dog after a Diet of Vegetable Food.

	per cent.
Example No. 14	9·87*
Example No. 15	25·30
Example No. 16	16·50

Average amount of amyloid substance yielded by the above three analyses 17·23 per cent.

* This liver not examined till one and a half hour after death.

The effect of giving an admixture of sugar with animal food is similar to that produced by a vegetable diet. The sugar employed in my experiments was the brown or moist sugar that is used for domestic purposes. Various devices had to be resorted to to get the animal to take it. The plan I found to succeed the best was to introduce it into short lengths of the small intestine forming part of the bundle of tripe. I will give the leading particulars belonging to each of the four dogs that formed the subjects of experiment in this way.

No. 17. A nearly full-grown mongrel dog, kept for eight days on a diet consisting of sugar and a bundle of tripe *per diem*. At first one-third of a pound of sugar was administered daily, but after three or four days the animal showed a disinclination for food, vomited, and had bilious diarrhœa. The quantity of sugar was reduced to a quarter of a pound daily. The dog now devoured voraciously all that was given to it. The urine collected from the bladder after death gave a strong reaction of sugar (grape-sugar).

No. 18. A youngish dog, fed for nine days on a bundle of tripe and a quarter of a pound of sugar daily. It consumed its food well at first, but during the last few days a great amount of coaxing was required to get it to take its full allowance. There was scarcely any urine to be procured from the bladder after death; what there was gave no saccharine reaction.

No. 19. A middle-aged dog, kept for eight days on a bundle of tripe and a quarter of a pound of sugar daily. The urine at death gave a slight but decided reaction of sugar.

No. 20. A dog not quite full-grown. Fed for five days on the same diet as the preceding dog. The urine collected after death gave a strong reaction of sugar.

The Liver of the Dog after a Diet of Animal Food with an Admixture of Sugar.

	Weight of dog.	Absolute weight of liver.	Relative weight of liver to animal.
	lbs. oz.	oz.	
Example No. 17	10 3	12	1 to 13¼
Example No. 18	11 14	12¾	1 to 14¼
Example No. 19	17 11	10¾	1 to 26
Example No. 20	12 0	13½	1 to 14
Total	51 12	49	1 to 16½

The average yielded by these four dogs gives a relative weight of liver bearing a close approximation to that after a diet of vegetable food; in the one case being as 1 to 16½, in the other as 1 to 15. The amount of amyloid substance in each case was large, as is shown by the following results of analysis:—

Amount of Amyloid Substance in the Liver of the Dog under a Diet of Animal Food and Sugar.

	per cent.
Example No. 17	12·80
Example No. 18	17·55
Example No. 19	12·33
Example No. 20	15·37

Average amount of amyloid substance yielded by the above four analyses 14·5 per cent.

The relative weight of the liver and the amount of amyloid substance present have varied much in the observations that I have made on the rabbit. But the better the condition of the animal, the larger is the quantity of amyloid substance its liver contains. In the two following experiments, the effect produced on the liver by a free administration of sugar and starch is strikingly corroborative of the results obtained upon the dog.

In one of the experiments, a couple of full-grown rabbits were taken as near as possible resembling each other. One was kept entirely without food; the other was fed daily for three days, through a tube passed down the œsophagus into the stomach, with one ounce of starch and three-quarters of an ounce of grape-sugar made into a semifluid mass with water. On the fourth day both animals were killed.

	Weight of animal. lbs. oz.	Weight of liver. oz.	Amount of amyloid substance. per cent.
Rabbit fasting	3 1	1¼	1·3
Rabbit on starch and grape-sugar . .	3 4	2¾	15·4

The other experiment was on two half-grown rabbits, likewise as nearly as possible resembling each other. One was made to fast, whilst the other was fed on an ounce of starch and the same quantity of cane-sugar daily for three days. On the fourth day the examination was made.

	Weight of animal. lbs. oz.	Weight of liver. oz.	Amount of amyloid substance. per cent.
Rabbit fasting	1 14	1	1·4
Rabbit on starch and cane-sugar . .	1 14¾	2⅜	16·9

I have a record of another experiment, but in this the amount of amyloid substance was all that was determined. The rabbit was allowed to take its ordinary food, and in addition, three-quarters of an ounce of loaf-sugar and half an ounce of starch were administered daily for three days. The animal was killed on the fourth day. The liver was not analysed until the day after death, but it then yielded 22·7 per cent. of amyloid substance.

After the administration of sugar, as in the above experiments, the liver is altered in its physical appearance. It becomes of a very pale colour, and so soft that it is readily

broken down by slight pressure between the fingers. I have seen it indeed so softened as to be almost pulpy, scarcely holding together when taken up by a pair of forceps.

I have made some analyses to show the relation that exists, in the transformation of amyloid substance into sugar in the liver after death, between the loss of the one and the gain of the other—how much sugar is formed for the hepatine that disappears. In the first three experiments, a part of the liver was instantly after death thrown into a freezing mixture, whilst the other was allowed to remain in the animal for some minutes. An analysis of the two specimens gave me the quantity of amyloid substance lost in the portion where the temperature was kept up, and likewise the amount of sugar that was formed. In the fourth, the liver was simply removed from the animal and examined at once, and then again in twenty-four hours' time.

	Amount of amyloid substance lost. per cent.	Amount of sugar gained. per cent.	Relation of gain of sugar to loss of amyloid substance.
No. 1	2·20	1·57	1 to 1·40
No. 2	7·04	4·25	1 to 1·65
No. 3	3·12	2·05	1 to 1·52
No. 4	1·82	1·12	1 to 1·62

Looking at the medium of these results, we get for the production of one part of sugar a loss of 1·54 of amyloid substance.

The following is a summary of the conclusions arrived at in this communication:—

The deductions drawn from an examination of the blood after death, without the observance of certain precautions, are fallacious. Blood collected ordinarily from the right side of the heart, after the destruction of life in a healthy animal, is strongly charged with sugar. This is not the condition naturally belonging to life; for if blood be drawn through a catheter from the right ventricle of a living animal which has remained in a quiescent state during the operation, it gives only a mere trace of the presence of sugar.

On suddenly destroying life, and instantly collecting the blood contained in the right side of the heart, it is found as free from sugar as if it had been collected during life.

From some recent carefully conducted experiments, the blood of the right side of the heart of an animal feeder is not distinguishable, as regards the amount of sugar present, from the blood of the portal vein.

Obstruction of the breathing determines an unnatural increase of sugar in the circulation, and a strongly diabetic state of the urine may be induced in this way.

The physiological or *ante-mortem* state of the liver, like that of the blood flowing from it, has been erroneously inferred, from the *post-mortem* condition that is presented. The liver at the moment of death is free, or almost completely free, from sugar, and the saccharine state which has been hitherto considered as belonging to it naturally during life, is in reality due to an easily recognizable chemical transformation which takes place with an astonishing rapidity after death.

The material existing in the liver, which is the source of the production of the sugar, is itself formed from sugar and its ally, starch. Dogs fed upon a diet abounding in starchy and saccharine materials have relatively very much larger livers, and livers strikingly richer in amyloid substance, than dogs fed upon a purely animal diet. In the rabbit fasting, the liver is exceedingly small and devoid of amyloid substance; whilst in the rabbit kept on starch and sugar only, the liver is large and exceedingly rich in amyloid substance.

In the transformation of amyloid substance into sugar in the liver after death, the production of one part of sugar is accompanied with the loss of 1·54 of amyloid substance as the average of four analyses.

XXVII. *On the Distribution of Nerves to the Elementary Fibres of Striped Muscle.* By Lionel S. Beale, *M.B., F.R.S., Professor of Physiology and of General and Morbid Anatomy in King's College, London; Physician to King's College Hospital.*

Received June 19,—Read June 21, 1860.

No branch of minute anatomy has received a larger share of attention than the anatomy of striped muscle, and probably no one point has been more carefully investigated than the distribution of nerve-fibres to this important tissue. Very different conclusions have been arrived at, and the various questions at issue have not yet been determined satisfactorily. For the different views entertained with reference to the mode of termination of nerve-fibres I must refer to the treatises on minute anatomy, and especially to Professor Kölliker's work just published, where a summary of the results of numerous investigations will be found.

Kühne's *Observations.*

The most recent observations are probably those of Kühne, who states that the nerve-fibre can be traced up to the sarcolemma. He concludes, with some other observers, that in the muscles of insects the axis cylinder of the nerve-fibre penetrates this transparent structure, and is connected with the rows of nuclei which are imbedded in the substance of the muscular fibre and lie amongst the fibrillæ*. As will be observed by reference to Kühne's drawings, these points are very indistinctly, and, if I may so say, diffidently represented. Like Kühne himself, I have quite failed to demonstrate in vertebrate animals the arrangement he described in insects. It may be remarked that nuclei amongst the fibrillæ are very abundant in some fishes and reptiles (especially the frog) whose muscles are sparingly supplied with nerves, while in the muscular fibre of many birds and mammalia which are very abundantly supplied, not a single nucleus can be demonstrated in the interior of the fibre. It seems hardly likely that the relation between the nerves and the contractile elements of the tissue should be closer in these cold-blooded, and comparatively inactive vertebrata, than in birds and mammals. The nuclei amongst the fibrillæ of the muscles of vertebrate animals are clearly not connected with nerves†.

* Untersuchungen über Bewegungen und Veränderungen der contraktilen Substanzen. Reichert and Dubois Reymond's (formerly Müller's) Archiv, 1860.

† Soon after this paper was read, I investigated the arrangement of the nerves distributed to the muscles of the larva of the common blow-fly and the perfect insect, and I have arrived at the conclusion that the nerves do not penetrate into the interior of the muscle, but are connected with some very large spindle-

General Opinion entertained.

The general opinion at the present time seems to be that nerves terminate upon the elementary fibres of voluntary muscle by free pointed extremities. KÖLLIKER considers it probable that the elementary fibres are only touched by the nerves at distant points, while some conclude that many fibres, or even parts of a muscle, are not brought into actual contact with nerve-fibres at all. As the results of my inquiries differ so entirely from those of other observers, I think it right to say that my observations have been very frequently repeated with great care, and upon several different vertebrate animals (man, dog, rat, guinea-pig, mouse, greenfinch, frog, tadpole, gudgeon, minnow, &c.). Several of the specimens from which my conclusions have been deduced are preserved permanently, and can be examined by all interested in this inquiry.

Of the Distribution of the Nerves to the Elementary Fibres.

My observations lead me to conclude that nerves are distributed to every elementary fibre of all voluntary muscles of man and vertebrate animals. The elementary fibres of some animals are much more abundantly supplied with nerves than those of others. The muscles of the mouse receive a larger supply than those of man. Generally, it may be said that the muscles of reptiles and fishes are sparingly supplied with nerves in comparison with those of mammals and birds. I have found that in the same animal a greater number of nerve-fibres are distributed to some muscles than to others. Thus the elementary fibres of the tongue of the mouse receive a larger supply than those of the diaphragm, and the latter a much larger supply than the muscles of the system generally.

The sarcolemma of the elementary fibre of the tongue and diaphragm of the mouse seem to be completely covered with nerves and vessels. The nerves for the most part run close to the capillaries, and it is not possible to separate these structures from each other without destroying them. Some of the nerve-fibres cross the elementary fibre transversely, others obliquely, while some run longitudinally on the central or lateral aspects of the fibre. In favourable specimens the nerves may be seen to divide on the surface of the sarcolemma. The ultimate fibres are, however, of such extreme delicacy, that a little careless manipulation, pressure, or a very slight alteration in the density of the fluid in which they are immersed, or in its refractive power, renders them quite invisible or destroys them altogether. I have not been able to follow an individual fibre for any great distance in consequence of the constant change in its course. These observations show that it is possible for an elementary fibre to be supplied with nerves from several different sources. It is not possible to decide, from the course of a single nerve-fibre, whether it is coming from, or passing towards, the nervous centre. Many fibres, apparently passing from one point, can be followed for some distance in opposite directions. The appearance of the nerve-fibres on the elementary muscular fibre differs

shaped cells on its surface. These are very difficult to demonstrate, but I have been able to preserve some specimens which show this point very clearly.

materially in certain cases. This seems to depend in some measure upon the state of the muscular fibre itself. If it is contracted, the nerve-fibres appear much wider than in cases where the muscle is relaxed and the fibres stretched to their full extent. The nerve-fibres undergo change very soon after death, and the finer ramifications seem to be completely destroyed by alkalies. Unless the tissue be properly preserved very soon after the death of the animal, it is not possible to demonstrate the arrangement described in this paper. The delicate structure very soon becomes destroyed by the action of air or water, and nothing is to be seen but a few oil-globules and a little fibrous-like structure.

The nerves of muscle freely divide and subdivide before they reach their ultimate distribution, as was demonstrated by WAGNER and others. I have observed that many of the ultimate fibres which appear to be single, really consist of two or more fibres in close apposition, which vary much in their diameter. Where one fibre is wide, its neighbour is reduced to a very thin cord. A little further on the diameter of the latter increases, while that of the former becomes reduced in a corresponding degree. A fibre passing into a trunk at right angles is frequently seen to divide into two branches which become lost in the trunk, but may be seen to pursue their course in opposite directions. The finest ramifications upon muscle are thin and flattened, as may be seen at points where the nerves pass round one elementary fibre to reach the surface of another.

Oval Bodies or Nuclei.

In connexion with all nerve-fibres, there are little oval corpuscles which are readily coloured by carmine. These are the nuclei of authors, and are essential constituents of the nerves, especially towards their peripheral distribution. They are soft in the recent state, and, in my preparations, have a granular appearance under the highest powers of the microscope. They contain two, three, or more distinct globules, with a clear outline and transparent centre, the so-called nucleoli. In ordinary dark bordered nerve-fibres, these bodies for the most part appear to be situated outside the white substance (nuclei of the tubular membrane); but in some nerves they may be seen in the white substance itself, and occasionally in connexion with the axis cylinder. As the nerves approach their distribution these bodies increase in number, and undoubtedly form an integral part of each separate fibre. They are often equal to the fibre in width, and sometimes they appear even wider, but this is probably due to stretching and alteration in the fibre itself. In bands composed of from five to eight or nine fibres, in the mouse, they are more than the thousandth of an inch apart, but in some of the terminal fibres they are as close as the two-thousandth of an inch. Not unfrequently four may be seen close together upon the surface of an elementary fibre.

After giving a full description of the corpuscles imbedded among the fibrillæ, as can be easily demonstrated in the large primitive fibres of the frog, Mr. BOWMAN states that in one instance he observed similar corpuscles on the exterior of a fasciculus in the chrysalis of the tiger-moth, but the relations of these were doubtful. He also noticed

similar corpuscles in the sarcolemma itself*. These bodies have since been considered to belong to the areolar tissue, but it is probable that at least a certain number of them are the same corpuscles which I have described as forming an integral part of the nerve-fibre in its ultimate distribution.

I have found the oval corpuscles present in great number in nerves of sensation, as well as in those of motion, and in the nerves distributed to vessels. They are very numerous in the nerve-fibres which supply the papillæ of touch and taste. I have lately succeeded in tracing nerve-fibres amongst the muscular fibres of the heart. For the most part the bundles of nerve-fibres pass with the vessel. The compound fibres divide and subdivide, and very minute fibres may be traced for a long distance. I believe that the branches of each nerve-fibre passing into the muscular substance are brought into relation with an immense number of the muscular fibres of the heart (or rather with a considerable expanse of the muscular structure) by means of the oval nuclei, which are seen at short intervals throughout the whole course of the nerves. The distribution of the ultimate branches of the nerves to the muscular fibres of the heart is now being investigated.

The nuclei are in all probability the exact points at which all the phenomena connected with the action of nerves at their peripheral distribution occur. These bodies are more numerous in the nerves distributed to the muscles of the tongue and diaphragm of the mouse than in those of other muscles. A greater number are found in connexion with the nerve-fibres of the mouse than in those of man. Generally, the nerves of mammalia and birds have a greater number of nuclei, which are separated from each other by shorter intervals than those of reptiles and fishes. As is well known, they are found all along the trunks of the so-called gelatinous fibres, and the same disposition is met with in the nerves distributed to vessels. I have seen them on branches of the sympathetic close to their origin from ganglia, on the branches in the ganglia, and in the so-called ganglion cells or vesicles. I may be permitted to state that I have made several observations which go far to convince me that the so-called gelatinous fibres, or fibres of Remak, are not composed of fibrous tissue merely, as is now generally believed, but are really nerve-fibres, as they were originally considered. The exact nature and arrangement of these fibres, however, require further investigation before I can arrive at definite conclusions.

The nuclei, in their general appearance, much resemble the oval corpuscles which are connected with the walls of capillaries, and which in many instances lie quite external to them; and not unfrequently, in the same situation, are also found the nuclei of fibrous tissue, those of fat vesicles and other bodies of the same character, or nearly so, the nature of which has not yet been satisfactorily determined. By some observers, all the above structures, as seen in uninjected preparations, have been called areolar-tissue-corpuscles, or connective-tissue-corpuscles (*Bindegewebe-körperchen*). The bearings of this very important question must, however, be deferred.

* Philosophical Transactions, Part II. 1840, p. 485.

I should state that the nerves and vessels may be stripped off the elementary fibre without difficulty. In this process the corpuscles external to the sarcolemma and in connexion with the nerves and capillaries are also removed. In the frog, the corpuscles which are so numerous amongst the fibrillæ remain, but in the delicate muscles of the mouse I have often observed that all traces of corpuscles are completely removed by this operation, there being, at least in many instances, none within the sarcolemma. From numerous observations I have come to the conclusion that the nerves, like the capillaries, always ramify only upon the outer surface of the sarcolemma, and do not penetrate this structure *.

Of the Manner in which Nerves terminate.

From the arrangements above referred to, it would appear that the nerves may be described as originating in a network, formed by the oval corpuscles being connected together by intermediate fibres. This network is in close relation with other elements of the tissue to which the nerves are distributed. The nerves grow as the adjacent textures grow; and in any form of fibrous tissue which has attained a certain degree of thickness, it is very difficult to demonstrate the delicate nerve-fibres running amongst the coarse fibres which interlace in all directions. They may, however, be traced out by the direction which the oval nuclei are seen to take†. The network is continually undergoing alterations by the formation of new nuclei and connecting fibres, and by the removal of old ones. From the connexion of this network with the nerve-fibres, it would seem to follow that an impression made upon a given portion of a sentient surface might be transmitted to the nervous centre by contiguous fibres, as well as by the one which would form, so to say, the shortest route; and it is possible that impulses to motion may be conveyed to muscular fibres by a more or less circuitous path, as well as by a direct one.

Of the so-called Tubular Membrane.

Nerve-fibres are imbedded in a clear transparent material, which completely surrounds large separate fibres, in the form of a membrane, as usually described (the tubular membrane of authors). In the finer divisions, however, several separate nerve-fibres, differing much in thickness, are enclosed in this structure, and when examined by a moderately high power (220 diameters), appear to form one fibre. Many such fibres, which seem to consist of a single fibre, in good specimens may be resolved by a twelfth (700 diameters) into two, three or more fibres.

Not unfrequently very narrow fibres may be traced for a long distance running close to an ordinary fibre imbedded in what would be called tubular membrane. I have seen

* It is probable that the nerves and capillaries are very intimately connected with the sarcolemma, and in some preparations one is almost led to conclude that the sarcolemma is itself composed of nerves, capillaries, and a small quantity of fibrous tissue connecting them.

† The determination of the connexions of the numerous nuclei is, as would be supposed, a very difficult matter. This difficulty, however, is greatly diminished by examining well-injected preparations, in which the nuclei connected with the capillaries can be easily distinguished from those belonging to the nerves.

branches, apparently proceeding from the axis cylinder, pass through the white substance and run parallel with the fibre for a long distance, then leave this fibre and pursue their course in close relation with another. This transparent tissue becomes much spread out as the nerve-fibres approach their distribution, and numerous delicate fibres, connected both with nerves and vessels, may be seen in it. This delicate texture might be described as a tissue in which the nerves and capillaries are imbedded. In conjunction with the nerves and capillaries, it forms an exceedingly thin expansion or membrane on the external surface of the elementary fibre. In some specimens it would appear that this is incorporated with the sarcolemma itself, but this point is doubtful. I have some preparations in which it certainly appears as if the injection had passed between this membrane and the sarcolemma, and, as before stated, I have certainly removed capillaries and nerves from the surface of the elementary fibre, leaving the sarcous material apparently invested with its sarcolemma; but this point is of course very difficult to demonstrate.

Of the Axis Cylinder and the White Substance.

I have been led to conclude that the axis cylinder divides and subdivides into many branches, so that one fibre in the trunk of a nerve may carry impressions to or from a comparatively large extent of surface. I have not yet been able to determine by actual observation if a branch of one axis cylinder may run in apposition with one or more branches from the axis cylinder of another trunk at a distance from the first, or derived from another source; but from appearances I have observed I think this possible. The axis cylinder often exhibits a tendency to split, but I have not yet been able to ascertain if it consists originally of a great many fibres which ultimately become fused into one, or of one fibre which gives off numerous branches; but from what I have seen, I feel sure that towards the distribution of the nerve the axis cylinder divides and subdivides very freely, the amount of investing substance which surrounds it (white substance of SCHWANN) becoming less and less, until in the finer ramifications it is not possible to say that a fibre consists of an axis cylinder and white substance; for its general appearance and refractive power are the same in every part, except where the nuclei are situated. The arrangement of the so-called tubular membrane has been already explained. It is not unreasonable to suppose that the definite character of the white substance of SCHWANN and the axis cylinder, in the larger nerve-fibres, results from changes which occur during the gradual growth and altered relations of the fibres which take place during the development and growth of the entire organism. The full discussion of these points demands a knowledge of the history of the development of the structures referred to. This we do not yet possess; but nevertheless I may perhaps be allowed to state briefly the conclusion to which I have arrived from investigations which, however, cannot be regarded as completely satisfactory. The axis cylinder, towards the ultimate ramifications of the nerve-fibres, loses its fibrous or band-like character, and in the ultimate subdivisions, the entire extent of the nerve-fibre possesses the same compo-

sition. There is no tubular membrane, medullary sheath or axis cylinder to be demonstrated; neither is there any definite point at which the so-called white substance can be said to cease. The axis cylinder gradually loses its hard fibrous character (frog), and the white substance its peculiar refractive power and consistence. The whole fibre, as seen in my specimens, seems to consist of a very transparent and perhaps delicately granular substance, which can be shown to be composed of fatty and albuminous material. These appearances, are, however, produced by the action of reagents (chromic acid, bichromate of potash); for in their natural state, at least with the aid of the object-glasses we possess at present, the finer ramifications of the nerve-fibres and their nuclei are quite invisible.

Of the Formation of New Fibres.

New branches are continually being developed in connexion with the terminal nerve-fibres, and a certain number of old ones appear to undergo removal. The oval bodies divide longitudinally and transversely, and the segment about to give rise to the new fibre is lengthened by elongation at each end, where the new fibre still remains in connexion with the original branch. Its nucleus divides transversely, and the length of the fibre thus goes on increasing. Traces of nerve-fibres which have ceased to perform any active office may be seen in the form of delicate fibres, which still remain in connexion with actual nerve-fibres. I am of opinion that the so-called connective tissue found in small quantity between the elementary fibres of muscle, and in some other situations, is produced in this manner. In many morbid alterations the so-called areolar, fibrous, or fibroid, or indeterminate connective tissue, certainly consists merely of the remains of other structures which have ceased to perform any active office, and cannot be completely removed by absorption.

Of Preparing the Specimens.

My specimens were obtained from preparations which had been previously injected with transparent blue injection. I found that without this operation it was not possible to follow the delicate nerve-fibres among the capillary vessels, or to distinguish these structures from each other with absolute certainty. I also adopted this plan as the only one calculated to introduce a preservative fluid simultaneously to all parts of a tissue, and with sufficient rapidity to prevent decomposition of the delicate structures under investigation. In this manner alone can alteration in chemical composition, in density and in refractive power of the preservative fluid employed, be prevented. The medium used was the same as that employed in my investigations on the anatomy of the liver*. Carmine solution was used for demonstrating the arrangement of the nuclei. The exact process employed is somewhat uncertain and complicated, and is probably capable of being rendered much more uniform in its results and more simple in its application.

* Philosophical Transactions, 1856. The principles on which this fluid is employed will be found stated in the 'Microscope in its application to Practical Medicine,' p. 63, and in papers published in the first volume of the 'Archives of Medicine,' 1859, pp. 18, 152.

Conclusions.

The most important facts which have been elucidated in this inquiry appear to me to be the following:—

1. That nerve-fibres in muscle and in some other tissues, if not in all, may be traced into, and are directly continuous with, a network formed of oval nuclei and intermediate fibres.

2. That the organs by which nerves are brought into relation with other textures, and the agents concerned in the development of nerves and the formation of new fibres, are the little oval bodies or nuclei which are present in considerable number in the terminal ramifications of all nerves. A great number of these bodies is associated with exalted nervous action, while, where sparingly found, we may infer the nervous phenomena are only imperfectly manifested.

3. That every elementary fibre of striped muscle is abundantly supplied with nerves, and that the fibres of some muscles receive a much larger supply than others.

4. That the nerves lie, with the capillaries, external to, but in close contact with, the sarcolemma. They often cross the fibre at right angles, so that one nerve-fibre may influence a great number of elementary fibres. There is no evidence of their penetrating into the interior of the fibre.

Explanation of the Plate.

PLATE XXIII.

Fig. 1. Nerve distributed to the elementary fibres of a muscle from the leg of a frog. To the right, two ordinary fibres and four finer ones are seen enclosed in the same transparent tissue (tubular membrane). As these subdivide, a division occurs in this structure, but many nerves, which to ordinary powers appear to consist of a single fibre, are found really to be composed of several individual fibres enclosed in one transparent sheath. At *a* is a fibre which is widest at that part of the nerve nearest to the nervous centre, while at *b* one is represented which is wider towards the peripheral extremity of the nerve. At the lower part of the drawing, two of the fine fibres have been pressed out of the transparent tissue, and one of them is broken off.

Fig. 2. Represents a portion of a compound fibre from the tongue of the frog. The branch from this (not more than $\frac{1}{1000}$th of an inch in diameter) is seen to contain three or four separate fibres; and it will be observed that, as this nerve passes to the larger trunk, fibres proceed from it which pass in both directions,—a fact which I have repeatedly observed in all the animals I have examined.

Fig. 3. Small portion of a fine nerve-fibre from the frog's tongue dividing into several separate branches. The subdivisions of the oval bodies are well seen.

Fig. 4. Small portion of a nerve, also from the tongue of the frog, showing several fibres contained in the same transparent tissue.

Fig. 5. Portion of a muscular fibre from the diaphragm of the mouse, showing nerve-fibres and capillary vessels. Below *a* is seen a fibre connected with the nucleus close to the capillary wall, but of the nature of this and of several similar fibres I have observed in connexion with the capillary walls, I am not certain. Oval bodies are seen apparently in the capillary walls, and also external to them. Some would refer the latter to the vascular nerves, and many appearances I have observed, some of which are delineated in my drawings, favour the idea that capillaries, as well as the small arteries, are supplied with nerves; but I am not yet able to express a positive opinion on this question.

Fig. 6. From the diaphragm of the mouse, showing the manner in which the finer bundles divide and traverse the elementary fibres in all directions. The intimate relation of the nerves to the capillaries is also shown in this drawing. In nature there is a delicate tissue connecting these structures together, so that they may be readily stripped off from the elementary fibre without injuring the latter.

Fig. 7. Portion of thin elementary fibres more highly magnified. At *a*, one of the oval bodies in process of subdivision is shown.

Fig. 8. Another portion, showing how the nerves vary in diameter in different parts. In the upper part of the drawing four large nuclei are seen close together.

Fig. 9. Two oval nuclei outside a capillary connected together by a fibre, with two nerve-fibres crossing a muscular fibre.

Fig. 10. A portion of a wide muscular fibre from the diaphragm of the mouse in a state of contraction. The nerve-fibre in the upper part is seen to divide.

Fig. 11. Fine nerve-fibre from the diaphragm of the mouse, under $\frac{1}{10,000}$th of an inch in diameter, but consisting of two, if not of three or more fibres.

Fig. 12. Another appearance frequently observed.

Fig. 13. Branching of very fine nerve-fibres from the tongue of the mouse.

Fig. 14. From the diaphragm of the mouse, showing the nerve-fibres between two elementary fibres of muscle.

Fig. 15. Also from the diaphragm, showing a portion of a muscular fibre nearly covered with nerves. Such specimens were common.

Fig. 16. Manner in which the oval bodies subdivide.

Fig. 17. Portion of a nerve-fibre undergoing increase in its length by the transverse division of the nucleus. From the surface of a muscular fibre from the diaphragm of the mouse.

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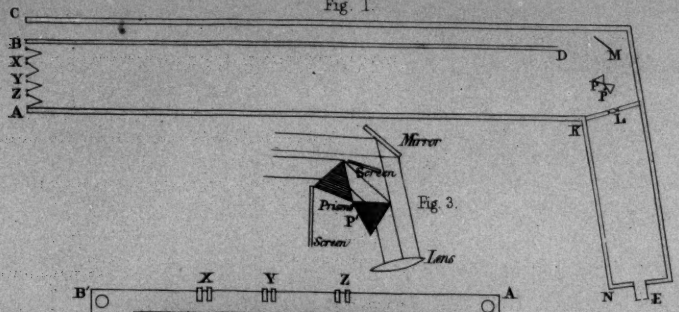

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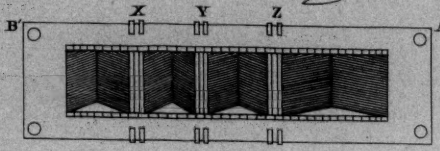

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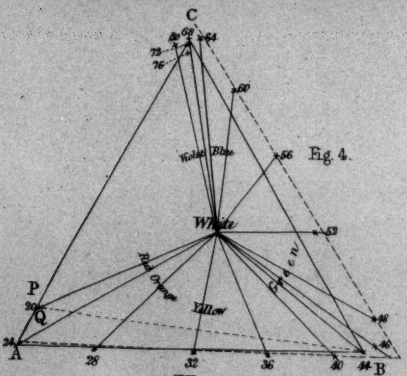

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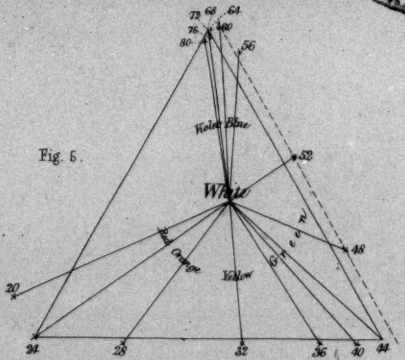

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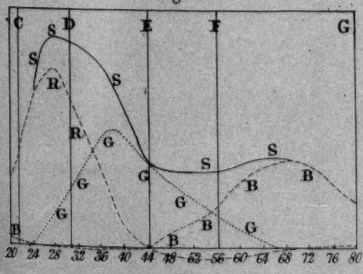

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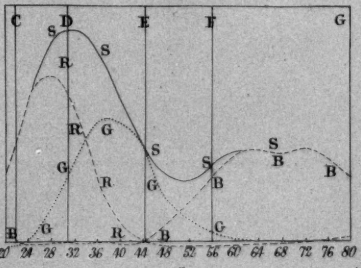

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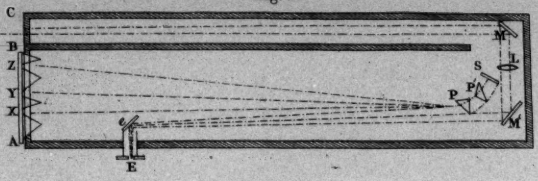

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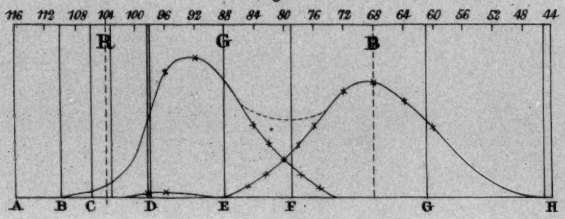


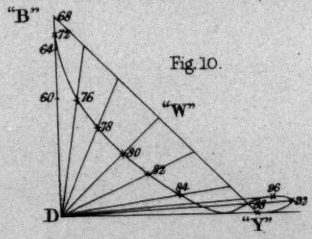


Fig. 10.

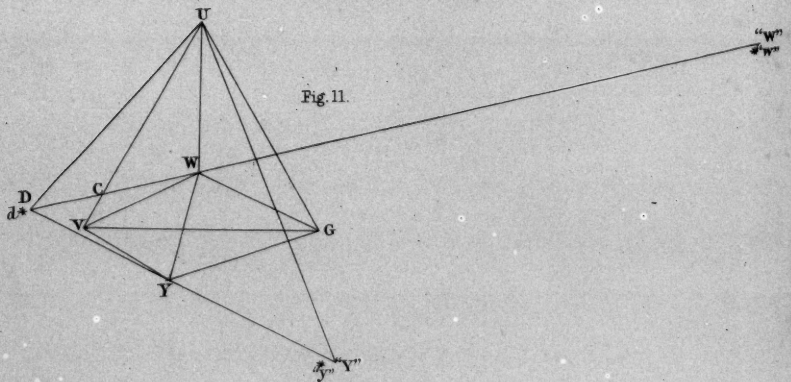


Fig. 11.

J. Basire, lith.

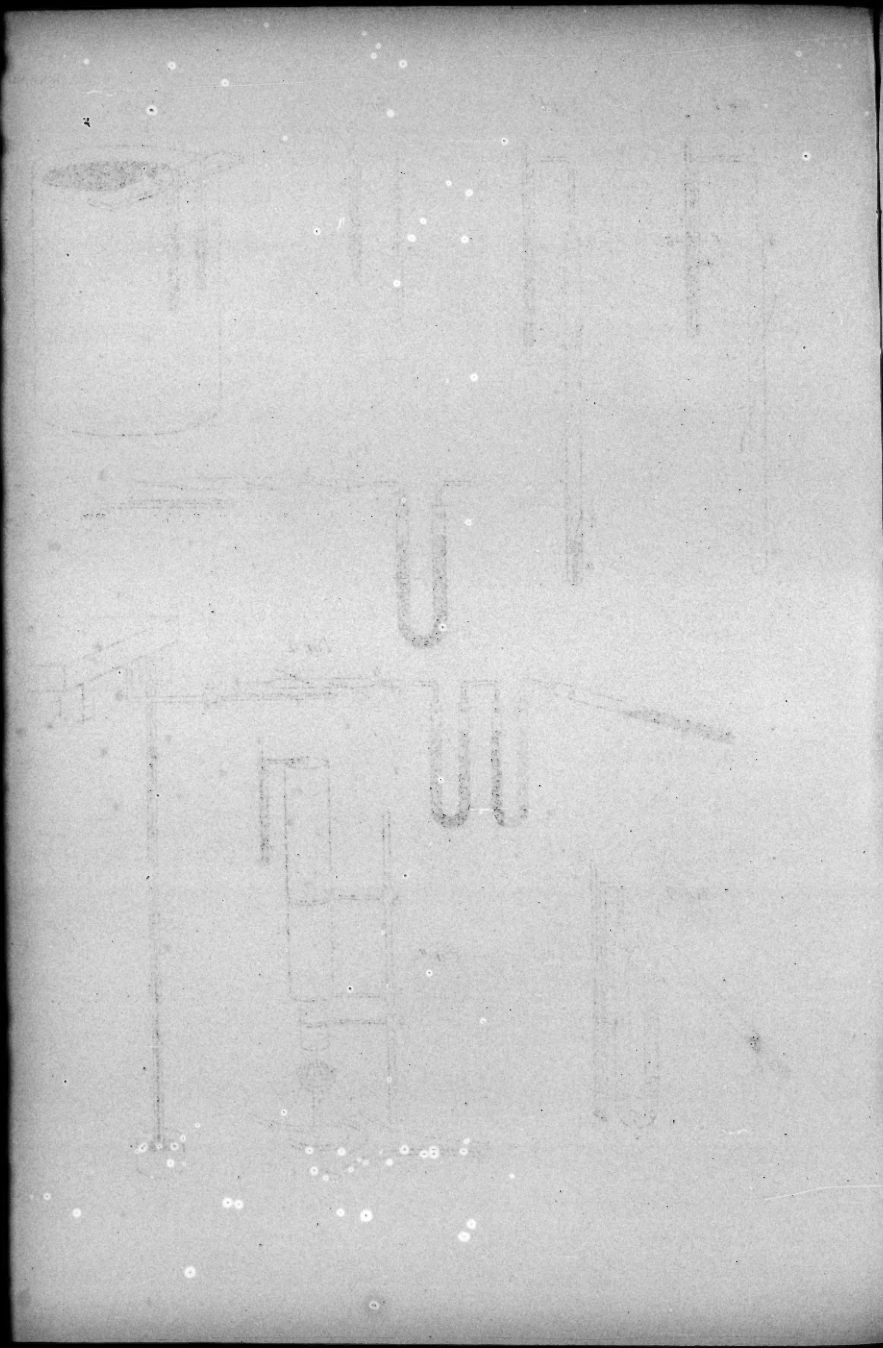


Fig: 1

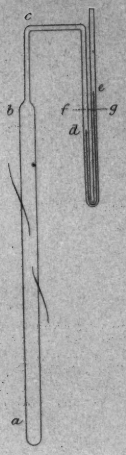
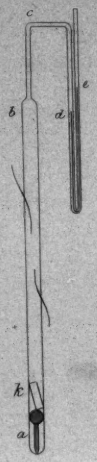


Fig: 1'



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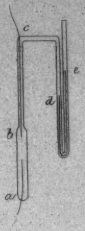

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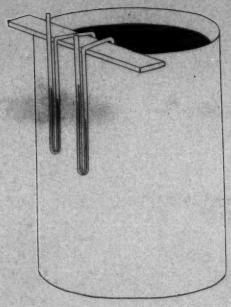

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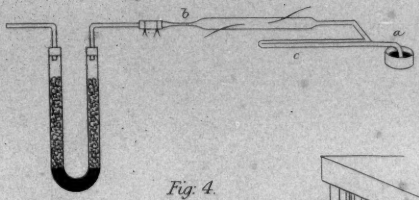

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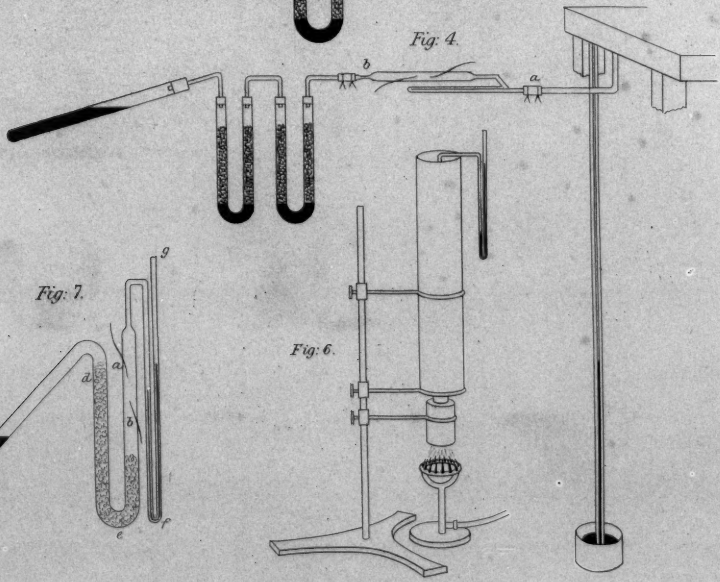
Fig: 4.



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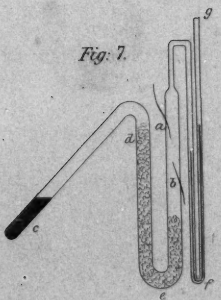


Fig: 6.

J. Basire sc.

Fig. 1.

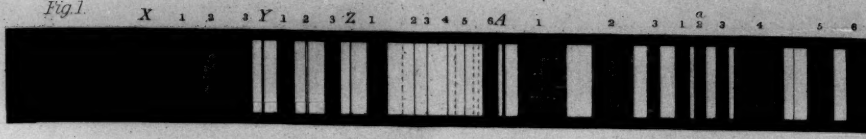


Fig. 1. Continued.

Fig. 2

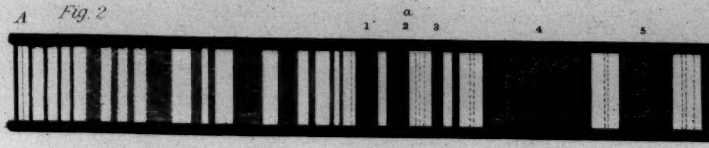


Fig. 6.

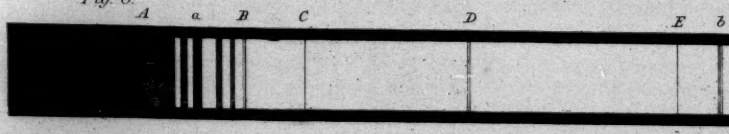


Fig. 7

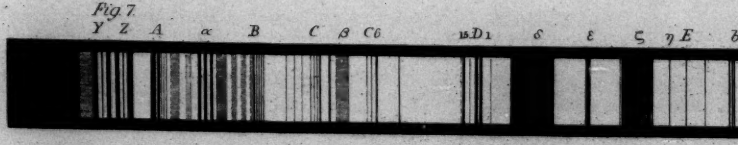
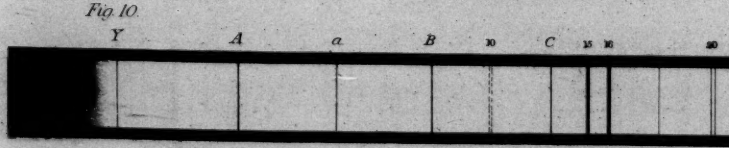


Fig. 10.



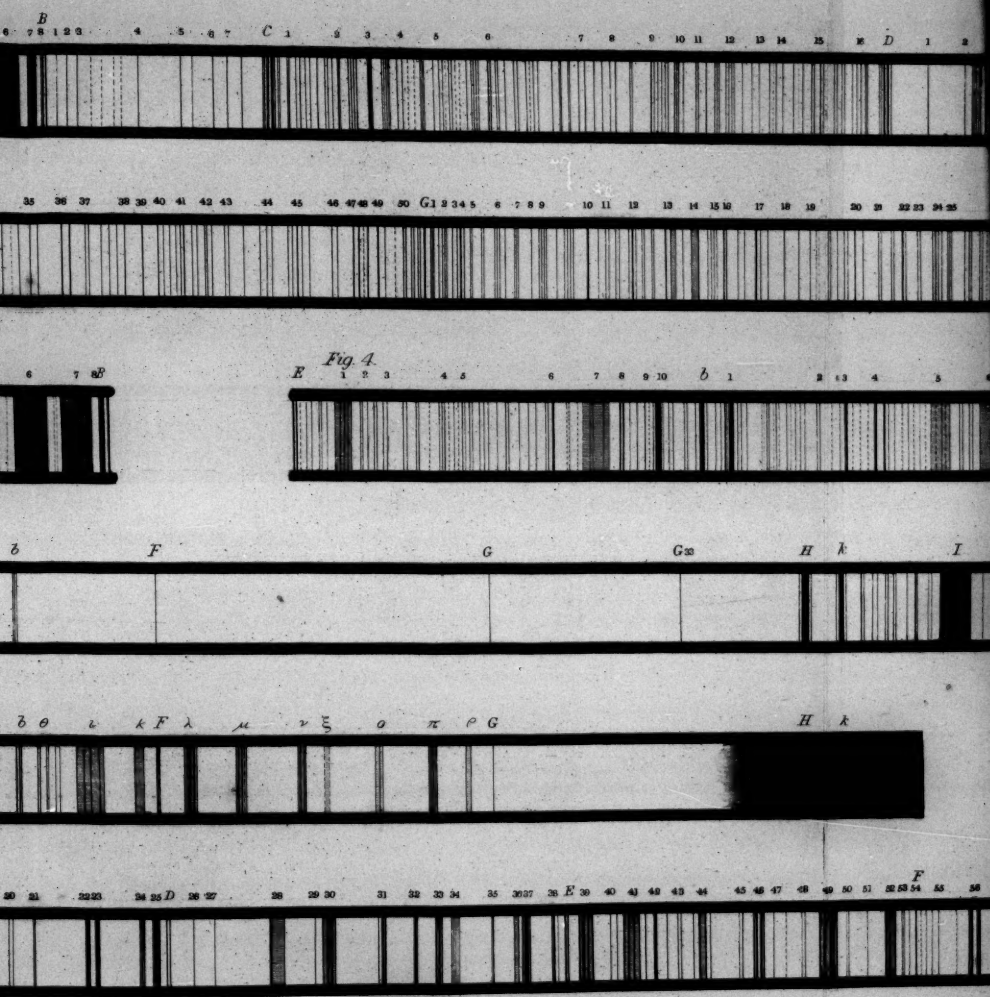


Fig. 4.

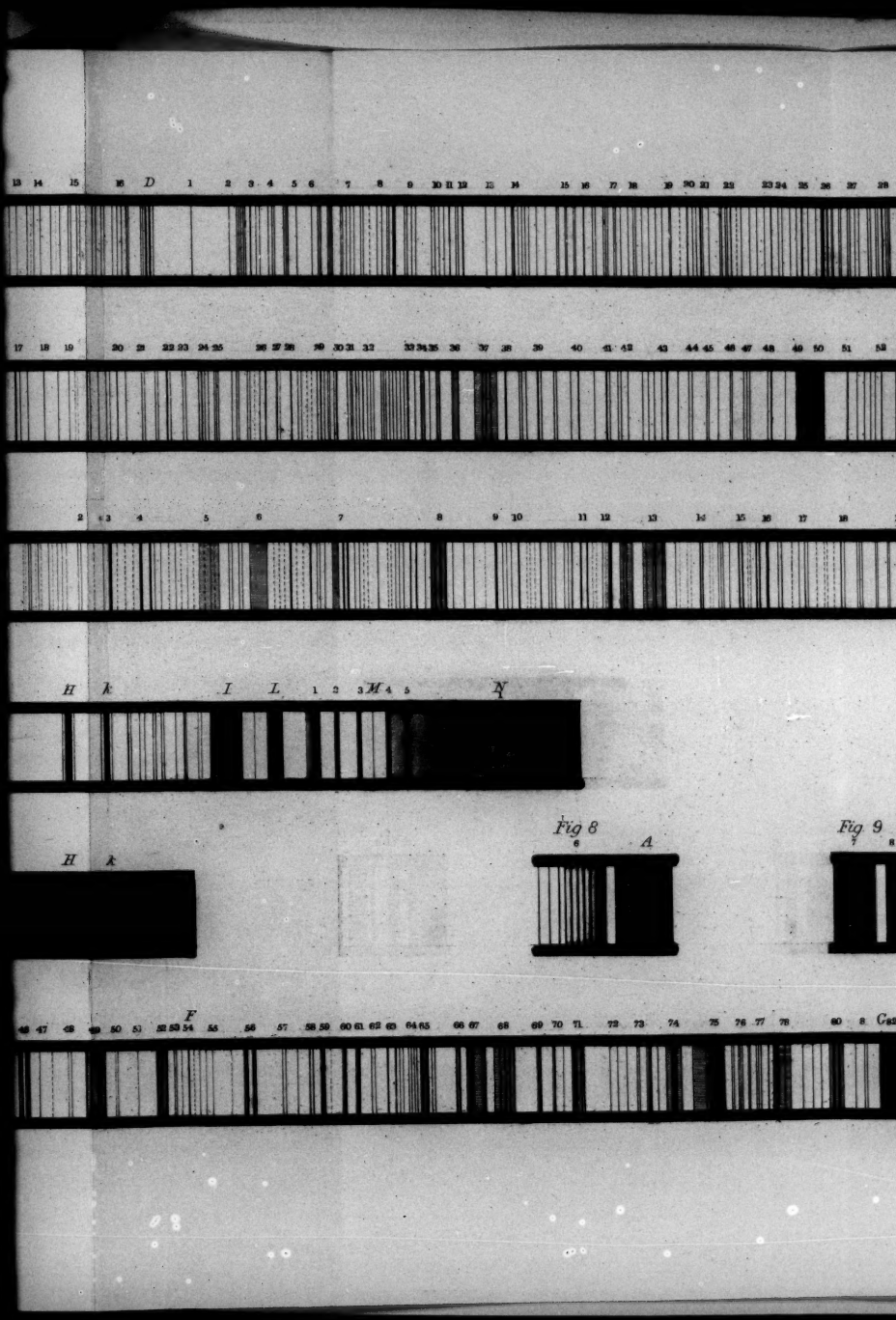

D
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Fig 8
Fig 9

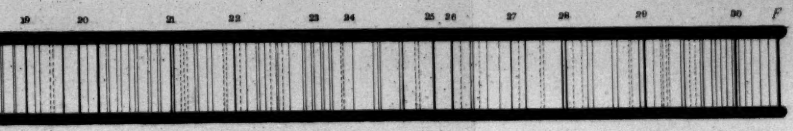

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Fig 3. a

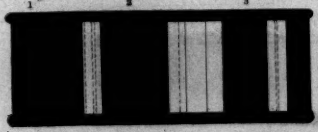
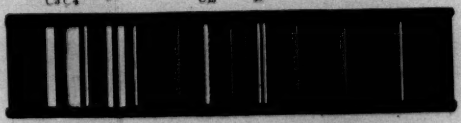
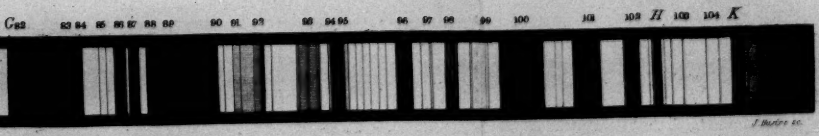


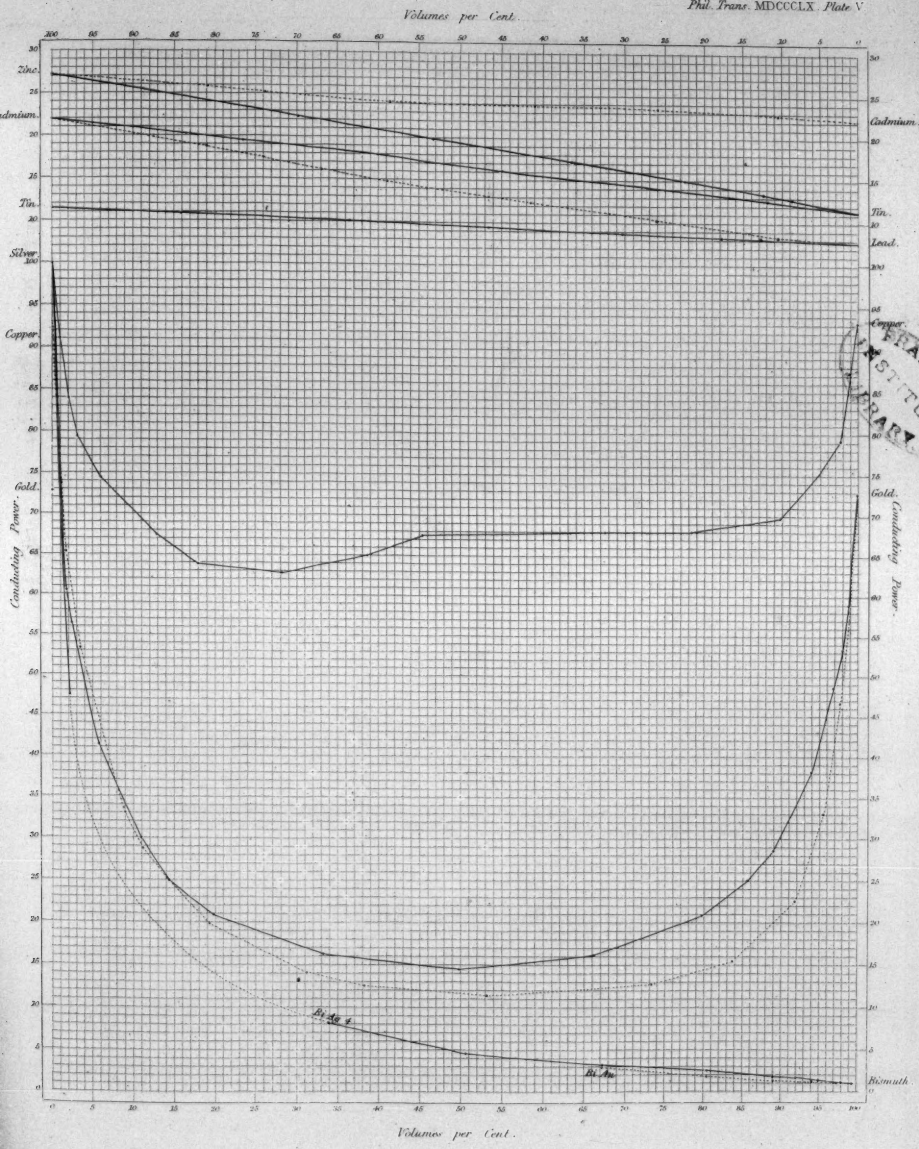
Fig 3. b

Fig 11





J. Basire sc.



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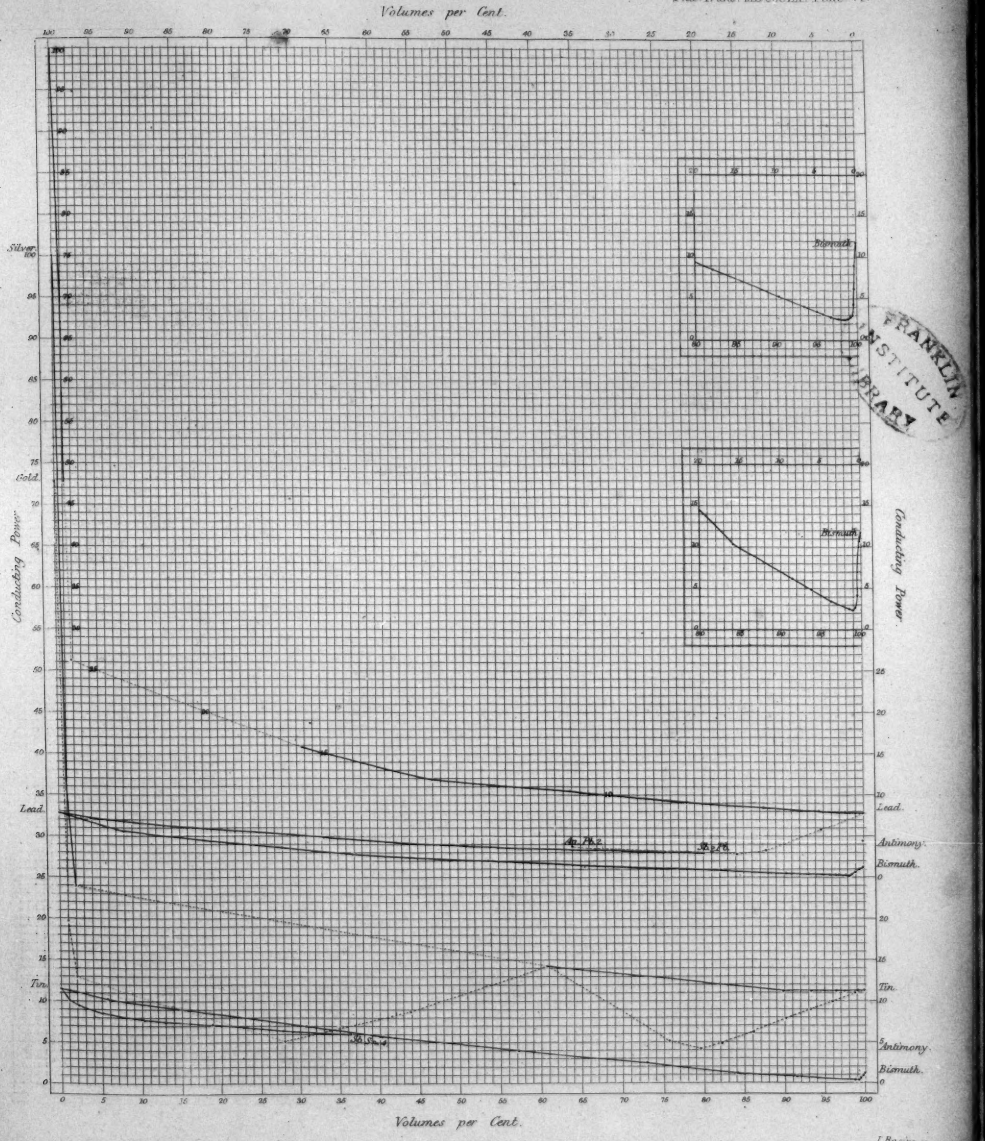

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Fig. 3.

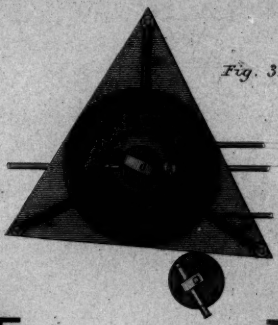
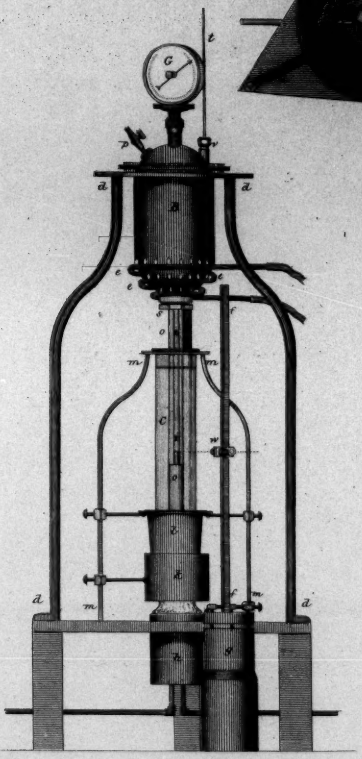


Fig. 1.



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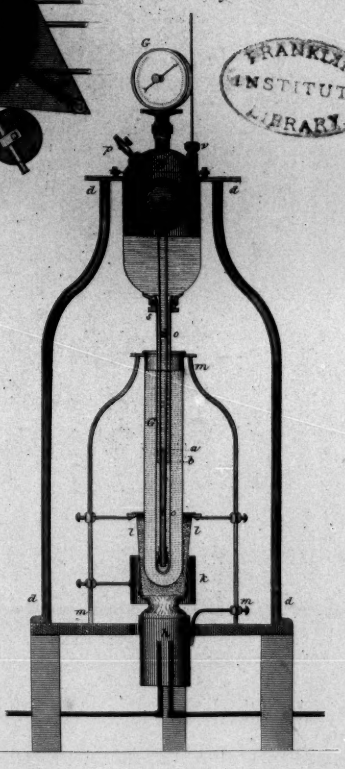

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APPARATUS

FOR EXPERIMENTS ON THE DENSITY OF STEAM AT PRESSURES

FROM 15 TO 70 LBS. PER SQ. IN.

Scale 1 inch to a foot

Basire sc.

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Fig: 2.

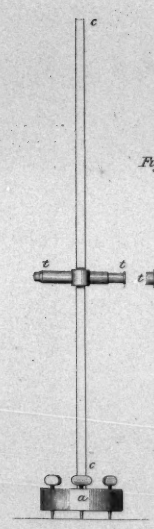


Fig: 3.

Fig: 1.

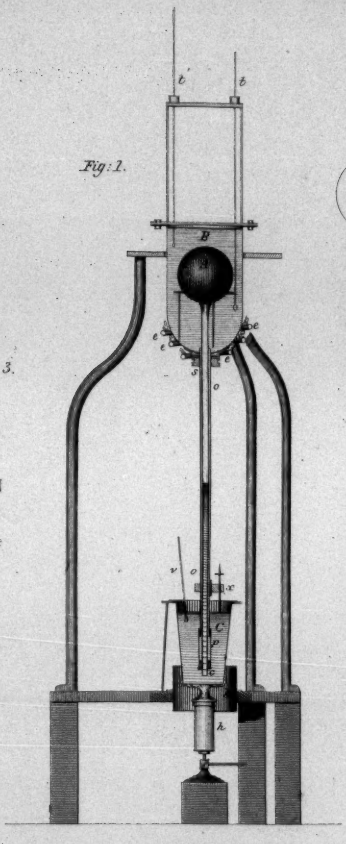


Fig: 6.

Fig: 7.

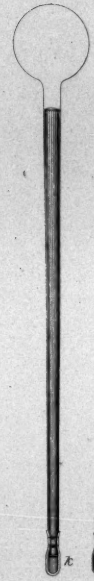


Fig: 4. Fig: 5. Fig: 8.

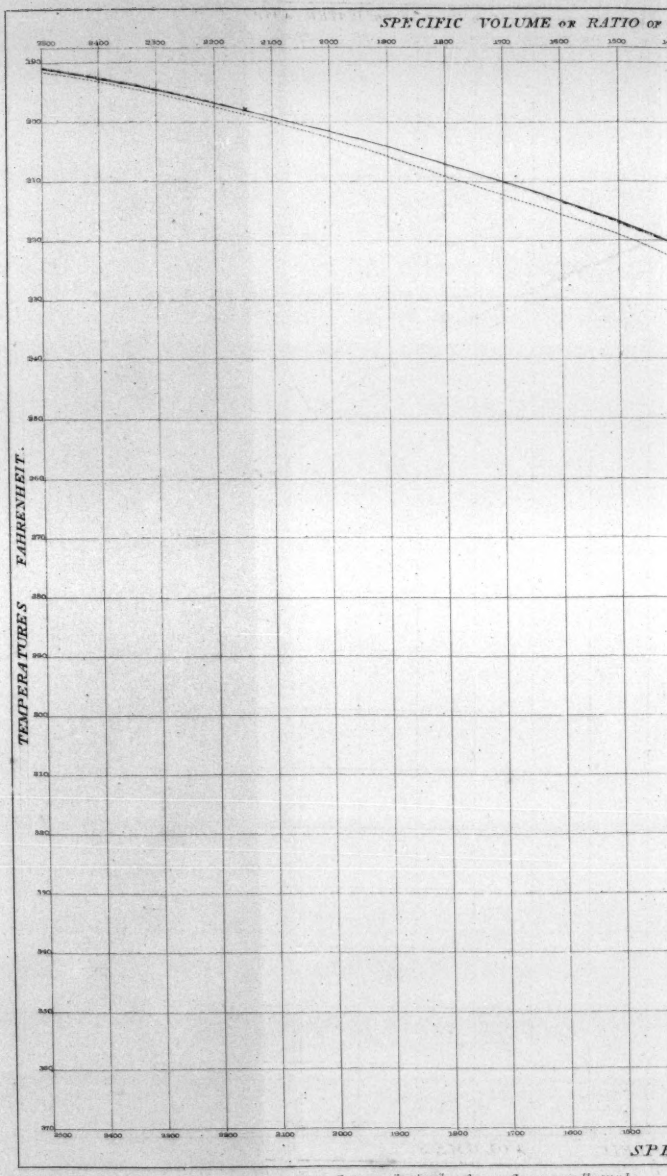
APPARATUS

FOR ASCERTAINING THE DENSITY OF STEAM

AT PRESSURES BELOW THAT OF THE ATMOSPHERE

Scale 1. inch to a foot.

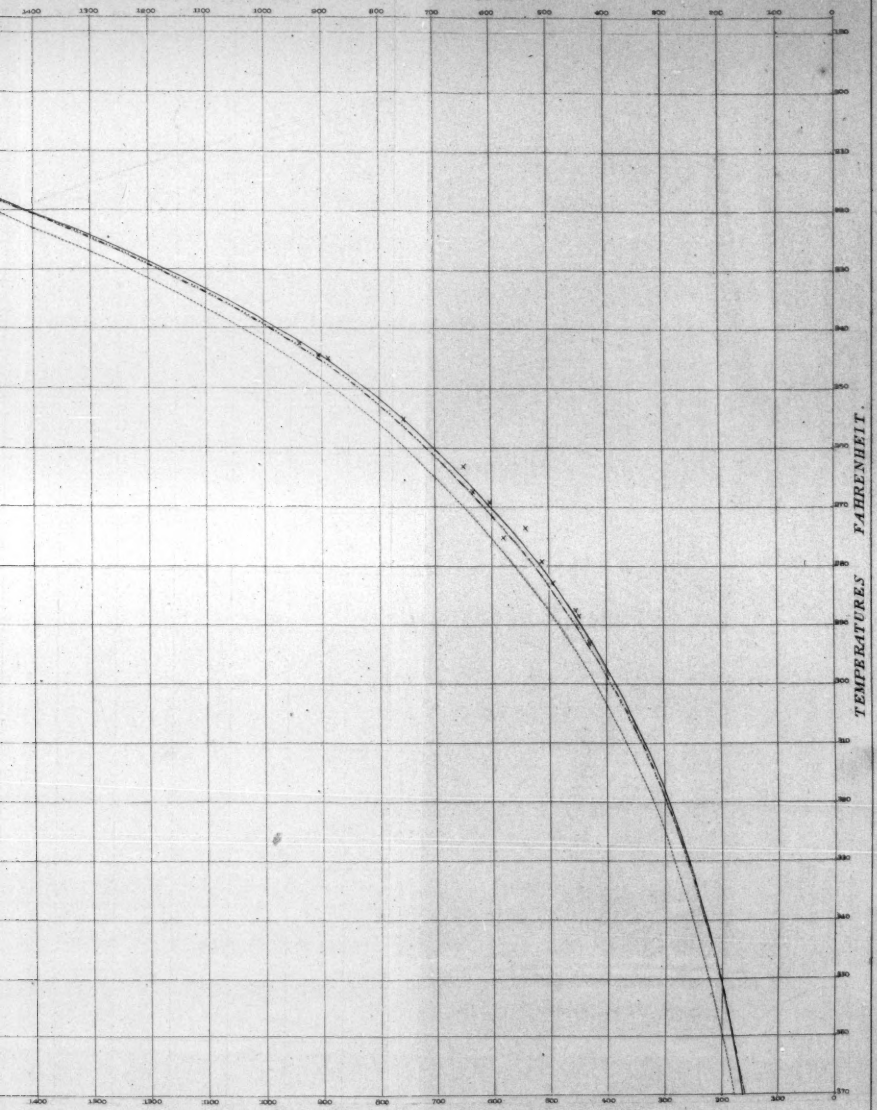
J.Basire, Sc.



Curve derived from Gaseous Formula.....

Note. This Plate does not include the Exper

OF VOLUME OF STEAM TO THAT OF THE WATER WHICH PRODUCED IT.



PECIFIC VOLUMES.

..... Curve from Experimental Formula. _____ Curve from M.r Rankines formula. _ _ _ _ _ _

periments at Low Temperatures. The Experiments are marked. ×

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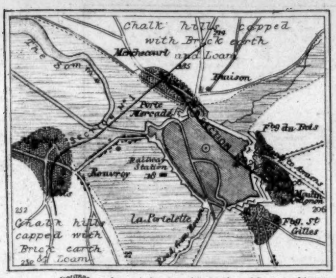
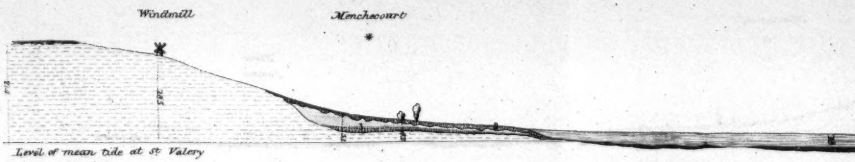
A. ABBEVILLE.



B. AMIENS.

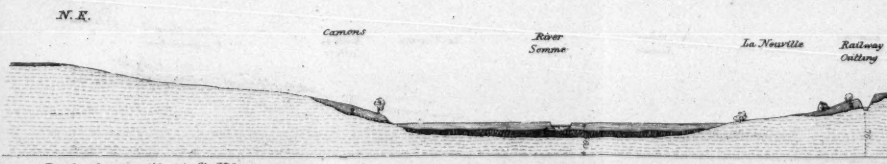
N.E.

1. SECTION ACROSS THE VALLEY



2. SECTION THROUGH ABBEVILLE

SECTION ACROSS THE VALLEY



1. Silt, Peat, & Gravel.

2. Brick-earth & angular flint-gravel

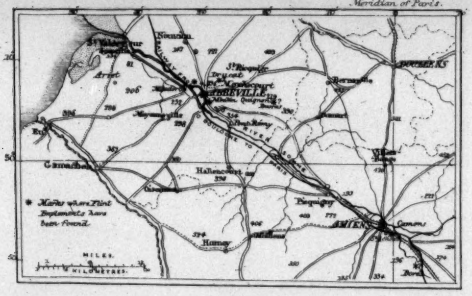
Verti

0 50 200

Horizon

PART OF THE DEPARTMENT OF THE SOMME.

Meridian of Paris.

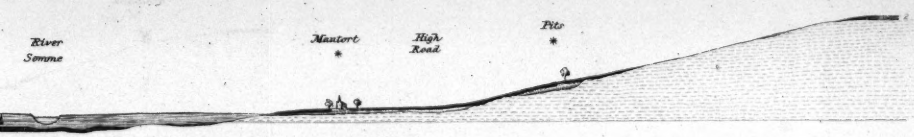


bove the Level of mean tide at St Valery.

Y OF THE SOMME AT ABBEVILLE.

S.W.

Hill on Road to Moyenneville

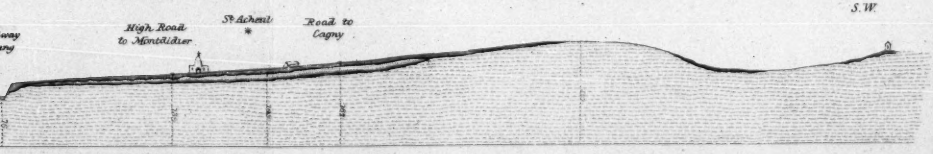


FROM MENCHECOURT TO MOULIN QUIGNON.

S.E.

Y OF SOMME AT AMIENS.

S.W.



rtical Scale.

200 300 400 500 Feet

zontal Scale

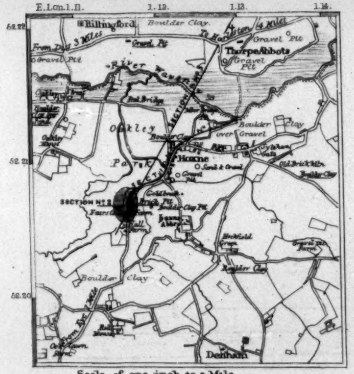
Mile

3. Fossiliferous sands, & gravel, with flint implements ab *

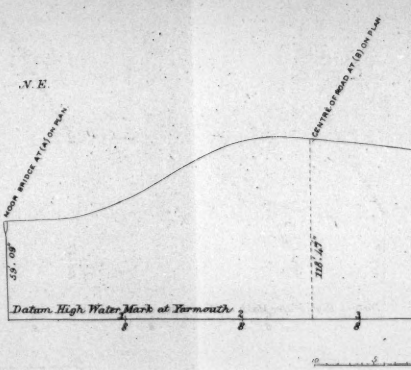
4 Chalk.

E Easton del

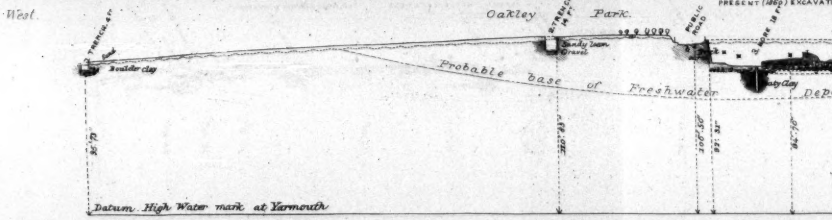
HOXNE, SUFFOLK.



1. LEVEL OF GROUND

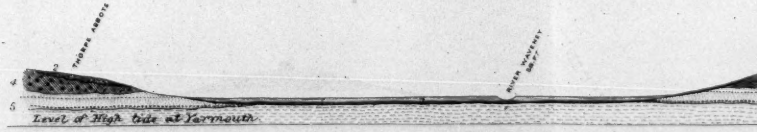


2. SECTION OF BRIC



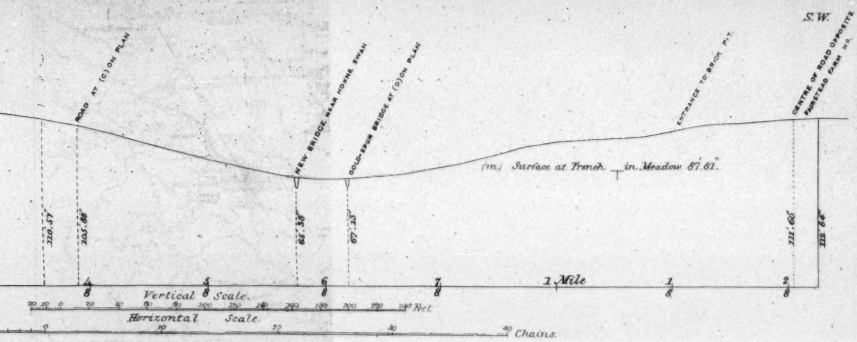
Flint Implements are found in b, k & c. (at x.)
Mammalian Remains ..... in b, c, & d.
Land & Freshwater Shells ... in d, & f.

3. SECTION ACROSS THE VALLEY



1 Silt, Peat, & Gravel.
2 Sand & Gravel.
3 Fossiliferous Clays & Gravels. with Flint Implements.

D FROM MOOR BRIDGE TO FAIRSTEAD FARM HOXNE.



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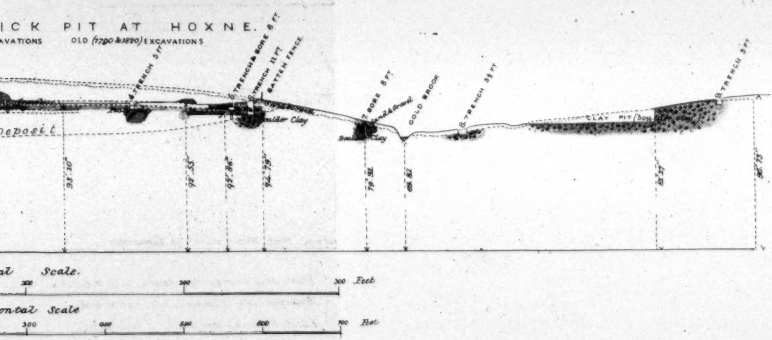
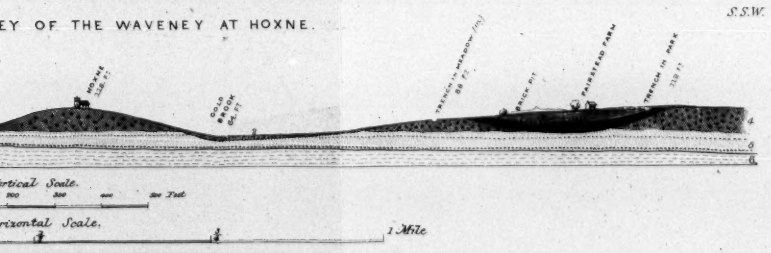
ICK PIT AT HOXNE.



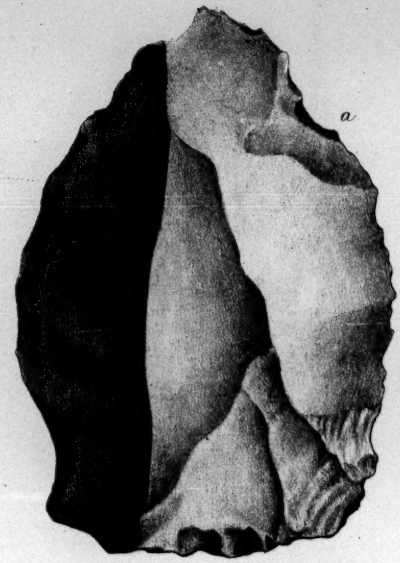
EY OF THE WAVENEY AT HOXNE.



4 Boulder Clay.
5 Sands & Gravels.
6 Chalk probable position of.

J. Basire sr.

Fig: 2.



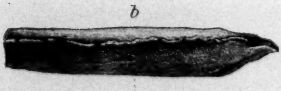


Fig: 3.

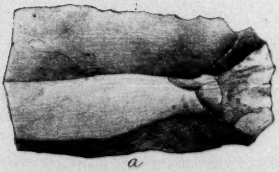
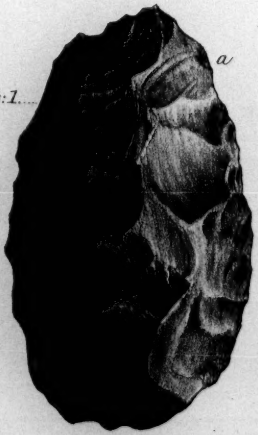


Fig: 1.



J. Scott, del.

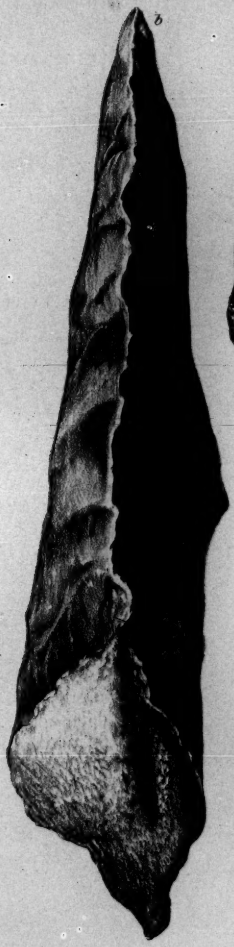
FLINT IMPLEMENTS.

Abbeville.

Actual Size.

J. Basire, lith.

Fig: 5.



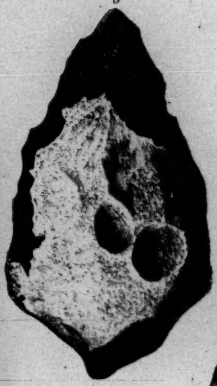


Fig: 4.

Fig: 3.

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J. Scott, del

J. Basire, Ju

FLINT IMPLEMENTS,

Amiens.

Actual Size.

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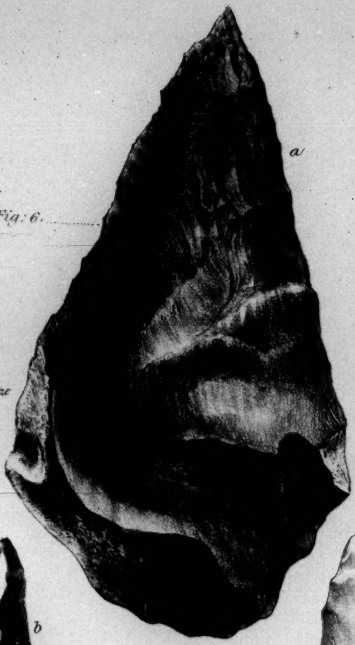
Fig: 6.



Actual Size

Fig: 7.

Scale $\frac{1}{2}$ Actual size.

Fig: 7.

Scale $\frac{1}{2}$ Actual size

Fig: 8.

Actual Size.

FLINT IMPLEMENTS.

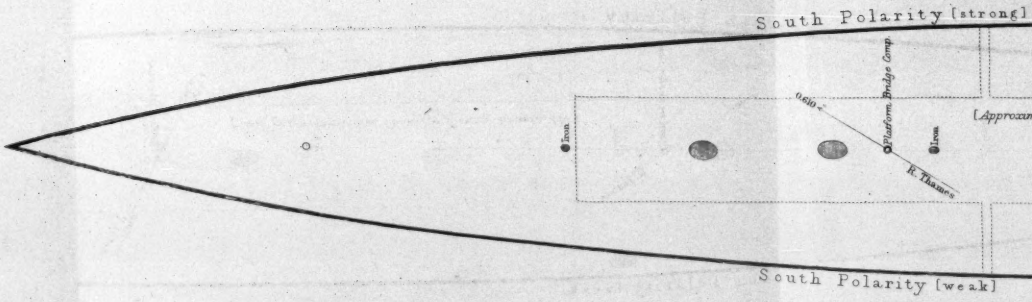
Fig: 6. Hoxne; Fig: 7. Abbeville. Fig: 8. Amiens.

J. Basire, lith.

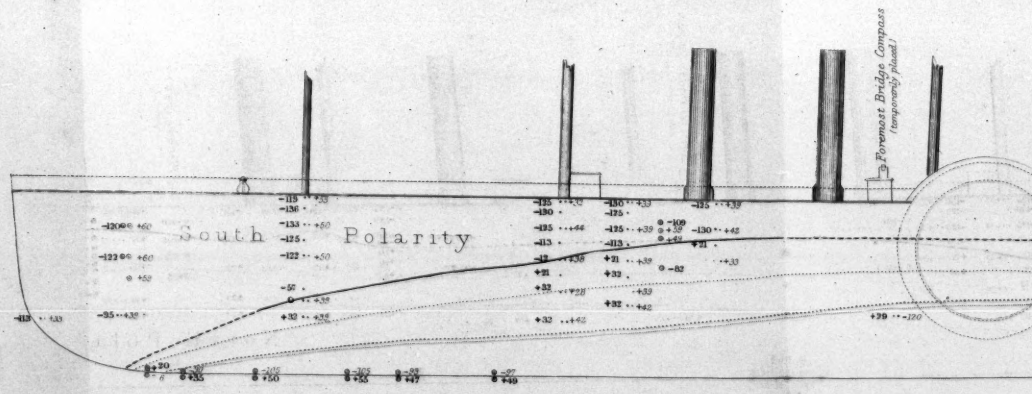
J. Scott, del.

IRON

GREAT



Sketch *shewing the Magnetic character of the topsides, the positions of the several Com*



Sketch of the S. S. Great Eastern, shewing the external ne

Note. *The broad continuous, and non-continuous lines, Septembe*
The small dotted lines, are approximately in November 1857

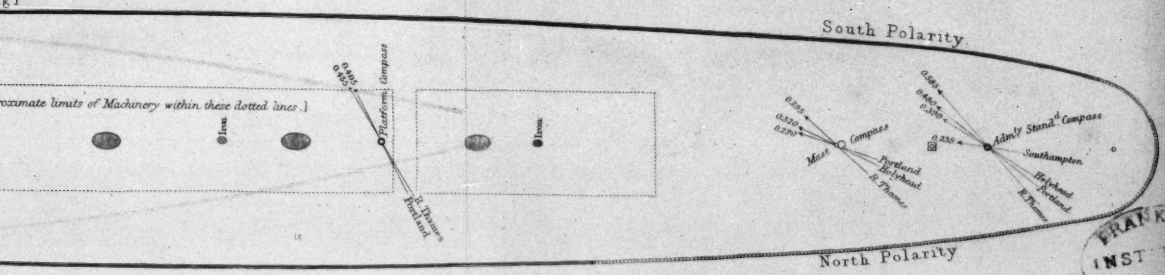
{Dark lines and figures, Port side of the Ship.
{Light ditto ....., Starboard .....

Deviation of the Compass (*in degrees*) {*The observations with a dot, (which denotes the position),*
{..... *encircled*

N STEAM SHIP

T EASTERN.

6]



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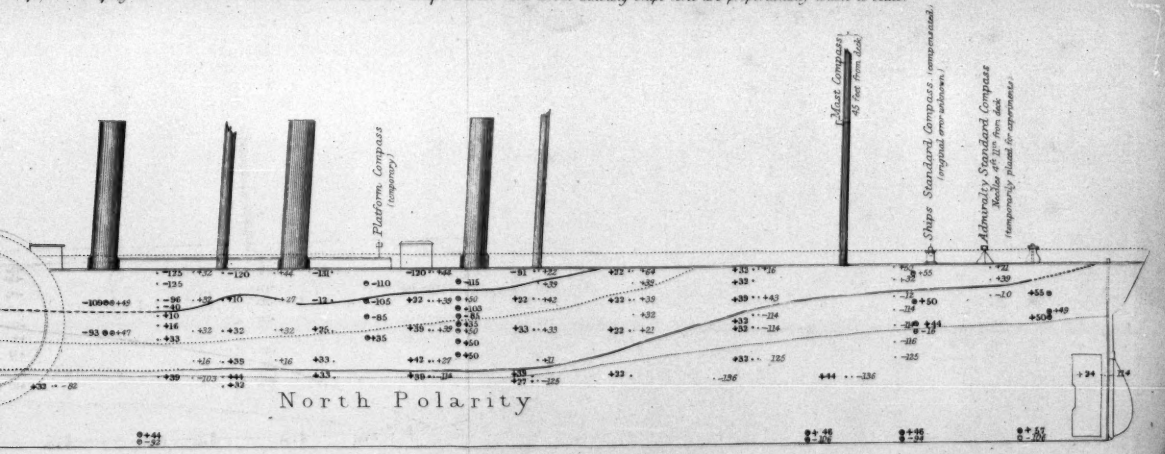
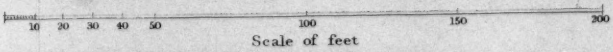
Compasses employed, and the direction and amount of Ships Force. (The arrows denoting Ships force are proportionally drawn to scale.)



neutral Magnetic Lines, or, the separation between the North & South polarity of the Hull.

nber 1.5, 1859, at Deptford.

857, prior to launching.



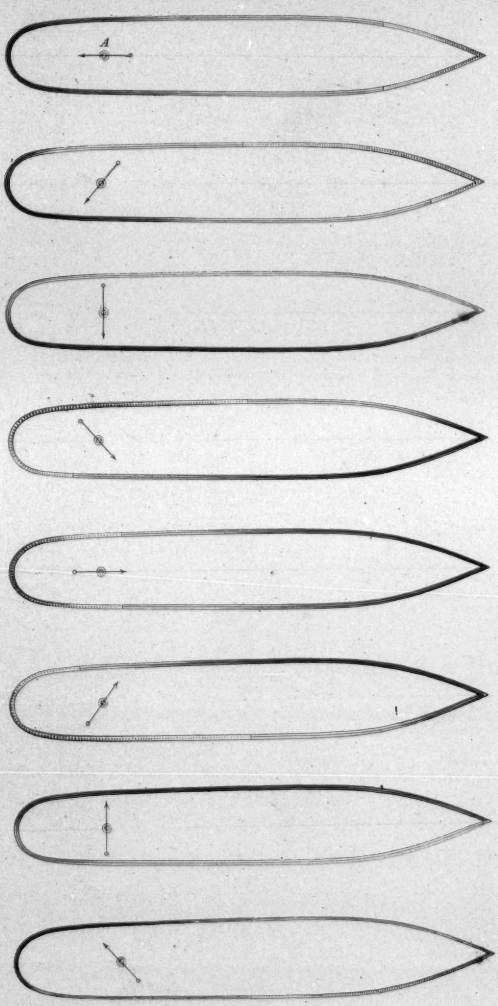
.), are those made in 1859 / 1857 (+ East Deviation, − West Deviation.

Direction of Keel and Head while building S. 29° 50' E. Mag.tic

at Deptford S. 46° 0' E.

J. Basire Sc.

Diagrams shewing Polarity of the topsides of an Iron vessel according to the direction in which her Head may be built with reference to the Magnetic meridian.



Head built.	Sign of Co-efficients B and C	
North	B	C
	−	0
N.E.	B	C
	−	+
East	B	C
	0	+
S.E.	B	C
	+	+
South	B	C
	+	0
S.W.	B	C
	+	−
West	B	C
	0	−
N.W.	B	C
	−	−

Note. { indicates South polarity (attracting north end of needle) } { The intensity of the shading a corresponding intensity of Magnetism.
{ indicates North polarity (repelling north end of needle) }

A, is the general position of the Standard Compass in Ships.
The Arrow indicates the direction of the Ships force.

J. Basire Sc.

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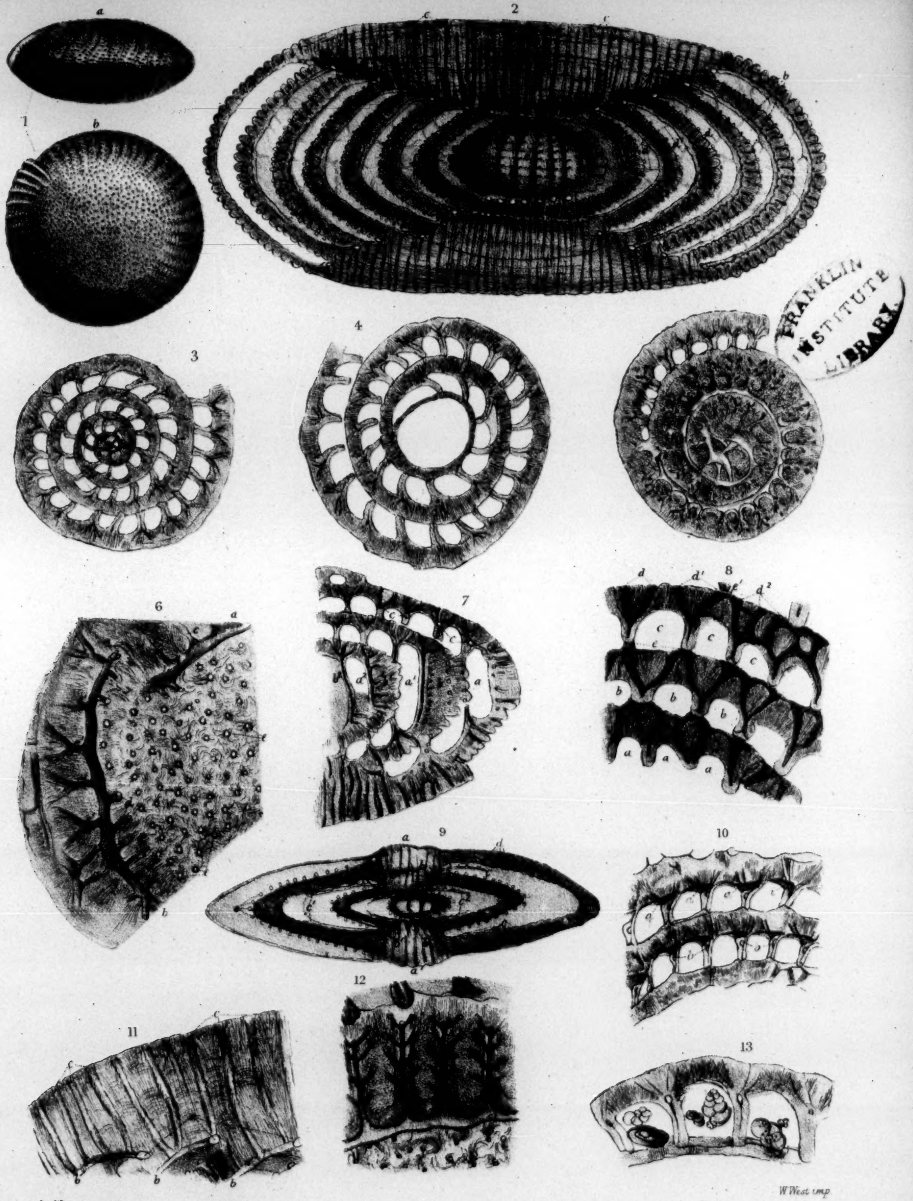

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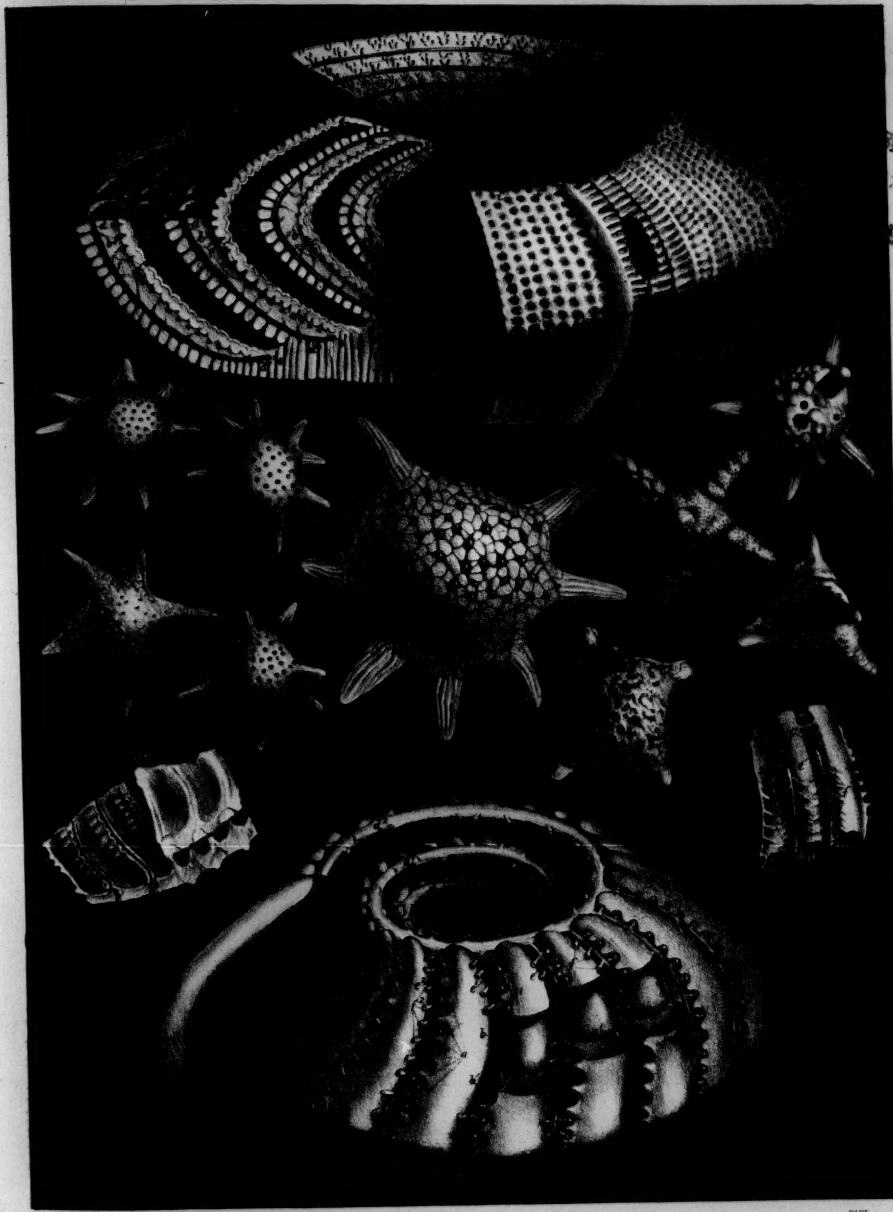
Geo West. del. et lith.

W West imp



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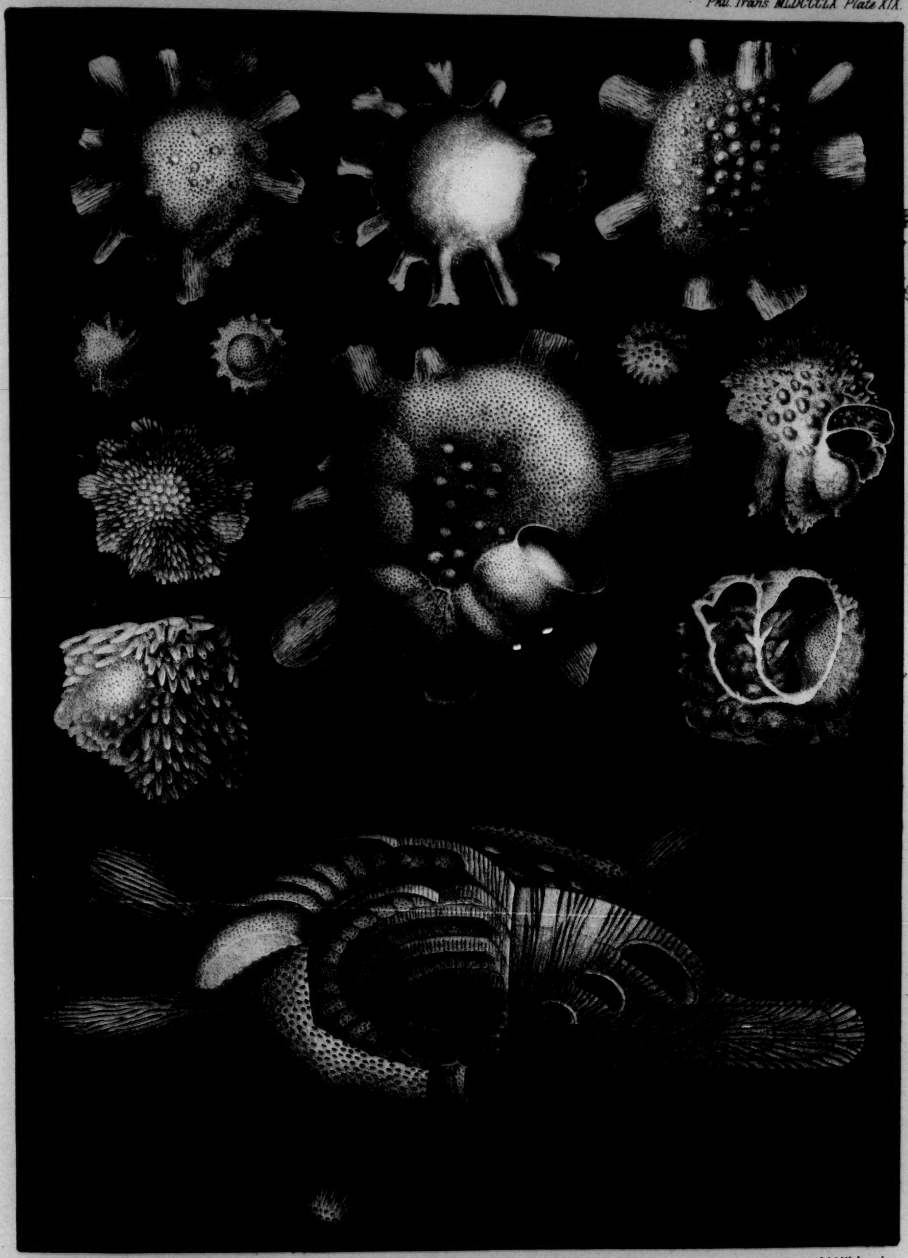
Geo. West. del. et lith.

W. West. imp.



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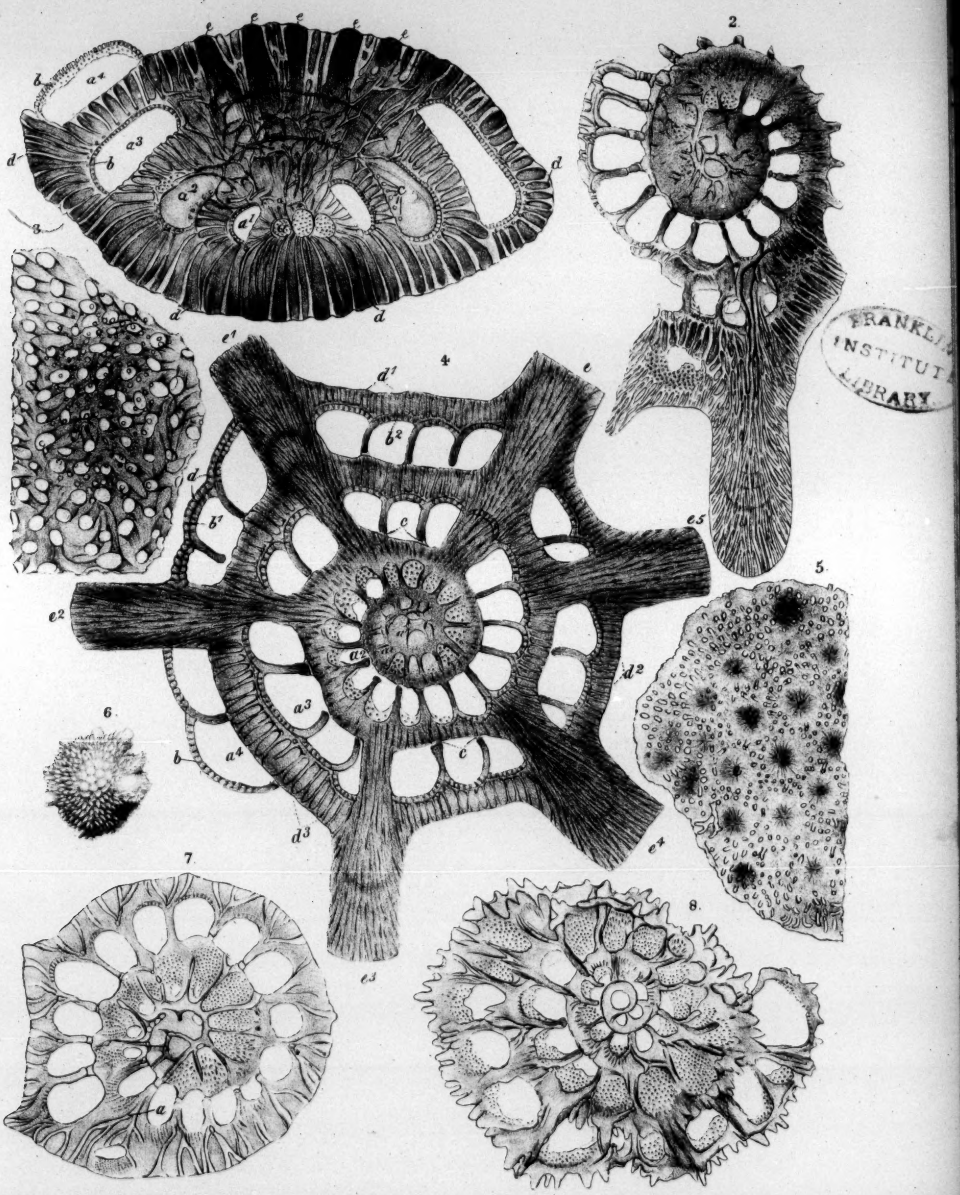
Geo. West del. Lens Aldous, lith.

Hullmandel & Walton, Imp.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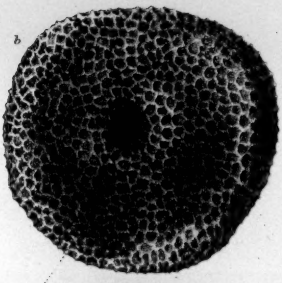

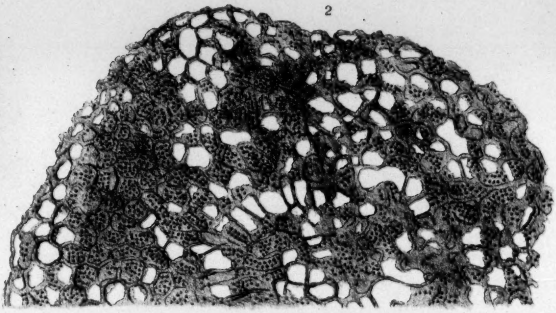

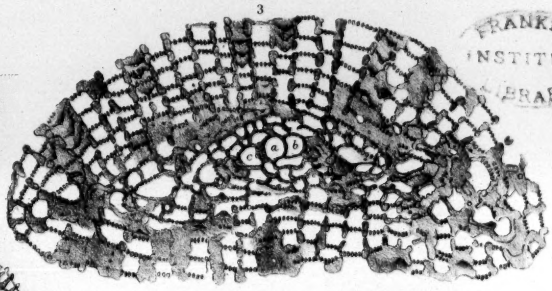

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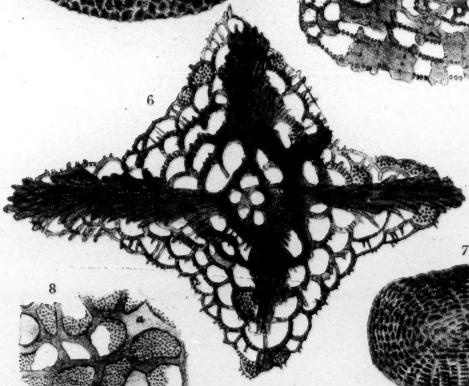

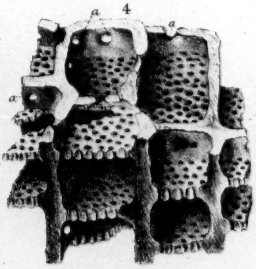

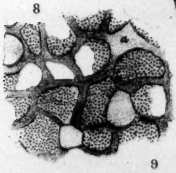

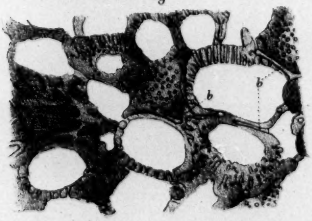

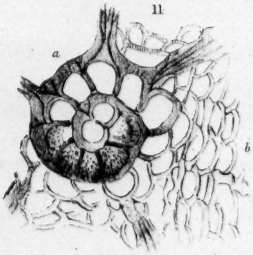

Geo West del. et lith.

W West. imp.

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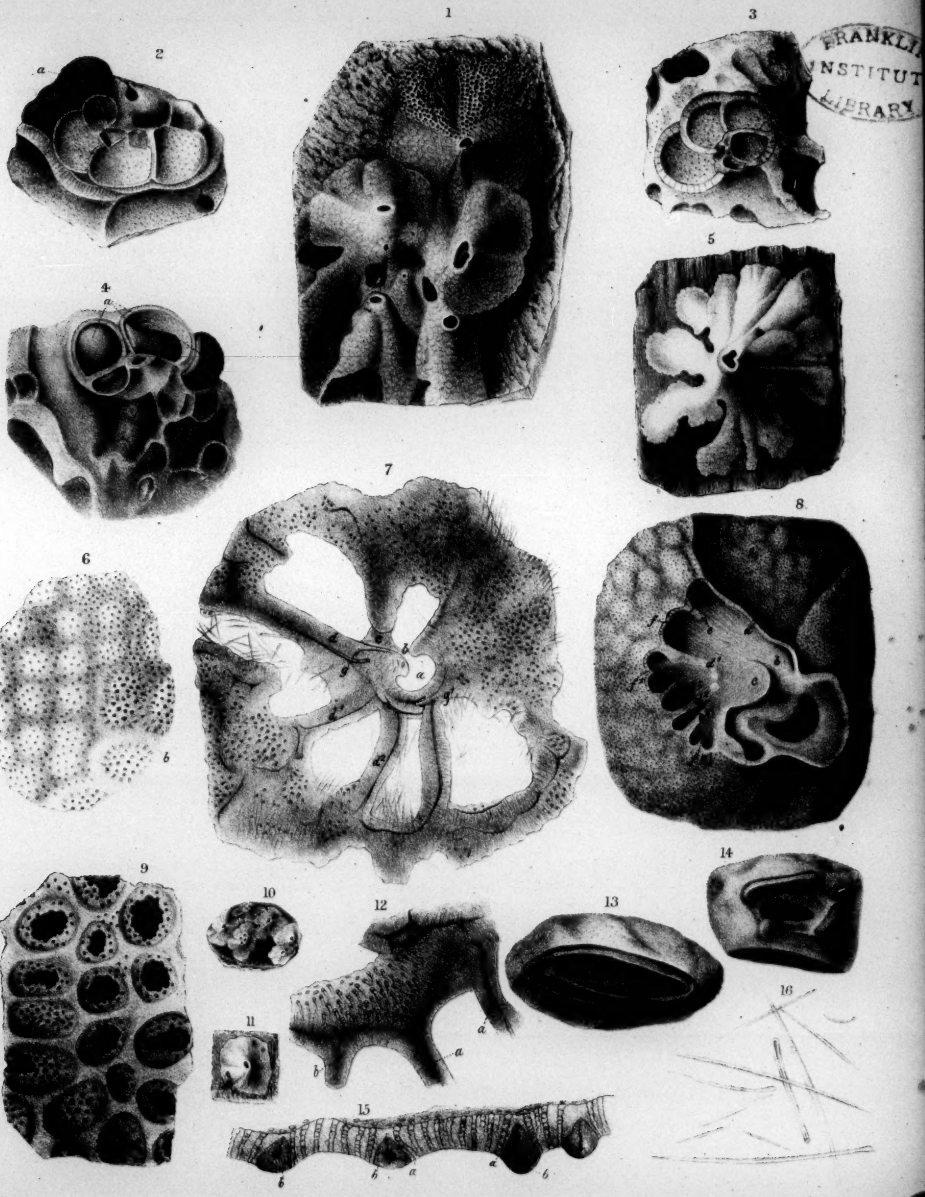
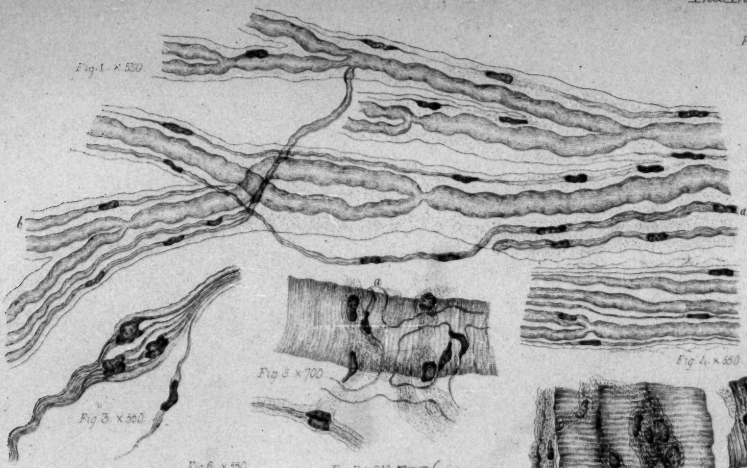


Geo. West del. Lane Allom lith.

Hullmandel & Walton, Imp.



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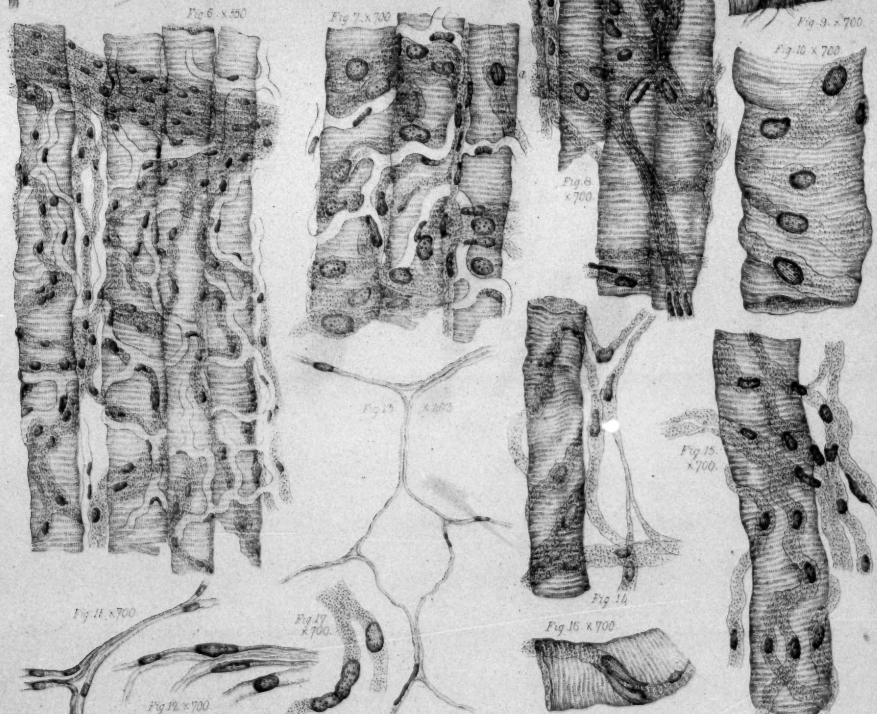

Lionel S. Beale ad. nat. del.

Edwin M. Williams, Sc.